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APPLICATION NUMBER: *60/405,220*
FILING DATE: *August 22, 2002*
RELATED PCT APPLICATION NUMBER: *PCT/US03/26326*

By Authority of the
COMMISSIONER OF PATENTS AND TRADEMARKS

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08/22/02 U.S. PTO

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PTO/SB/16 (10-01)
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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53 (c).

Express Mail Label No.	EU140615518US

PTO U.S. 60/405220 08/22/02

INVENTOR(S)		
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☒ *Additional inventors are being named on the 2 separately numbered sheets attached hereto*

TITLE OF THE INVENTION (500 characters max)

COBALT-SUBSTITUTED CHROMIUM OXIDE COMPOSITIONS, THEIR PREPARATION, AND THEIR USE AS CATALYSTS AND CATALYST PRECURSORS

Direct all correspondence to: **CORRESPONDENCE ADDRESS**

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ENCLOSED APPLICATION PARTS *(check all that apply)*

☒ Specification *Number of Pages* 62 ☐ CD(s), Number
☒ Drawing(s) *Number of Sheets* 4 ☐ Other (specify)
☐ Application Data Sheet. See 37 CFR 1.76

METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT

☐ Applicant claims small entity status. See 37 CFR 1.27.
☐ A check or money order is enclosed to cover the filing fees

FILING FEE AMOUNT ($)

☒ The Commissioner is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number: 04-1928 — 160.
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The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

☒ No.
☐ Yes, the name of the U.S. Government agency and the Government contract number are: _____.

Respectfully submitted,

SIGNATURE Dal E Hsr Date 08/22/02

TYPED or PRINTED NAME DAVID E. HEISER REGISTRATION NO. (If appropriate) 31,366

TELEPHONE 302 892 1926 Docket Number CL2099 US PRV

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

This collection of information is required by 37 CFR 1.51. The information is used by the public to file (and by the PTO to process) a provisional application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the complete provisional application to the PTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, Washington, D.C., 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Box Provisional Application, Assistant Commissioner for Patents, Washington, D.C. 20231.

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Docket Number	CL 2099 US PRV

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Patent fees are subject to annual revision.

☐ Applicant Claims small entity status. See 37 CFR 1.27

TOTAL AMOUNT OF PAYMENT ($) 160

Complete if Known	
Application Number	UNKNOWN
Filing Date	HEREWITH
First Named Inventor	V.N. MALLIKARJUNA RAO
Examiner Name	UNKNOWN
Group / Art Unit	UNKNOWN
Attorney Docket No.	CL2099 US PRV

METHOD OF PAYMENT *(check all that apply)*

☐ Check ☐ Credit card ☐ Money Order ☐ Other ☐ None

☒ Deposit Account

Deposit Account Number: 04-1928

Deposit Account Name: E. I. du Pont de Nemours and Company

The Commissioner is authorized to: *(check all that apply)*

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FEE CALCULATION

1. BASIC FILING FEE

Large Entity Fee Code	Large Entity Fee ($)	Small Entity Fee Code	Small Entity Fee ($)	Fee Description	Fee Paid
101	740	201	370	Utility filing fee	
106	330	206	165	Design filing fee	
107	510	207	255	Plant filing fee	
108	740	208	370	Reissue filing fee	
114	160	214	80	Provisional filing fee	160

SUBTOTAL (1) ($) 160

2. EXTRA CLAIM FEES

			Extra Claims		Fee from below	=	Fee Paid
Total Claims		-20	0	X	18	=	0
Independent Claims		-3	0	X	84	=	0
Multiple Dependent	☐			X	280	=	0

Large Entity Fee Code	Large Entity Fee ($)	Small Entity Fee Code	Small Entity Fee ($)	Fee Description
103	18	203	9	Claims in excess of 20
102	84	202	42	Independent claims in excess of 3
104	280	204	140	Multiple dependent claim, if not paid
109	84	209	42	** Reissue independent claims over original patent
110	18	210	9	** Reissue claims in excess of 20 and over original patent

SUBTOTAL (2) ($) 0

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FEE CALCULATION (continued)

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Large Entity Fee Code	Large Entity Fee ($)	Small Entity Fee Code	Small Entity Fee ($)	Fee Description	Fee Paid
105	130	205	65	Surcharge - late filing fee or oath	
127	50	227	25	Surcharge - late provisional filing fee or cover sheet	
139	130	139	130	Non-English specification	
147	2,520	147	2,520	For filing a request for reexamination	
112	920*	112	920*	Requesting publication of SIR prior to Examiner action	
113	1,840*	113	1,840*	Requesting publication of SIR after Examiner action	
115	110	215	55	Extension for reply within first month	
116	400	216	200	Extension for reply within second month	
117	920	217	460	Extension for reply within third month	
118	1,440	218	720	Extension for reply within fourth month	
128	1,960	228	980	Extension for reply within fifth month	
119	320	219	160	Notice of Appeal	
120	320	220	160	Filing a brief in support of an appeal	
121	280	221	140	Request for oral hearing	
138	1,510	138	1,510	Petition to institute a public use proceeding	
140	110	240	55	Petition to revive – unavoidable	
141	1,280	241	640	Petition to revive – unintentional	
142	1,280	242	640	Utility issue fee (or reissue)	
143	460	243	230	Design issue fee	
144	620	244	310	Plant issue fee	
122	130	122	130	Petitions to the Commissioner	
123	50	123	50	Processing fee under 37 CFR 1.17(q)	
126	180	126	180	Submission of Information Disclosure Stmt	
581	40	581	40	Recording each patent assignment per property (times number of properties)	
146	740	246	370	Filing a submission after final rejection (37 CFR § 1.129(a))	
149	740	249	370	For each additional invention to be examined (37 CFR § 1 129(b))	
179	740	279	370	Request for Continued Examination (RCE)	
169	900	169	900	Request for expedited examination of a design application	

Other fee (specify) _____

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SUBMITTED BY				Complete *(if applicable)*	
Name (Print/Type)	ELLIOTT A. KATZ	*Registration No Attorney/Agent)*	26,396	*Telephone*	302 992 4924
Signature				Date	AUGUST 22, 2002

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TITLE

COBALT-SUBSTITUTED CHROMIUM OXIDE COMPOSITIONS, THEIR PREPARATION, AND THEIR USE AS CATALYSTS AND CATALYST PRECURSORS

FIELD OF THE INVENTION

This invention relates to chromium-containing compositions and their preparation and use for the catalytic processing of hydrocarbons and/or halogenated hydrocarbons.

BACKGROUND

It is well known that α-Cr_2O_3 and α-Fe_2O_3 have in common the structure of α-Al_2O_3 (corundum) with the M^{+3} ions occupying octahedral sites in the hexagonally close-packed oxide lattice. In contrast, CoO has a lattice similar to NaCl while Co_3O_4 has a normal spinel structure. These basic structures are described in standard treatises; see, for example, pages 538, 543-545, and 550 of *Structural Inorganic Chemistry* by A. F. Wells, 5th ed. Clarendon Press, Oxford, UK (1986). γ-Chromium oxide ($CrO_{2.44}$) is described in Wilhelmi, *Acta Chemica Scandinavica*, Vol. 22, pages 2565-2573 (1968).

Numerous mixed metal oxides have been prepared in which the cation sites of the lattice are occupied by different metal ions. For example, solid solutions of the type $(Cr_xFe_{1-x})_2O_3$ are known where $0 < x < 1$. These materials have been prepared by standard ceramic or sol-gel techniques as described by Music, et al. in *J. Materials Science,*Vol. 31, pages 4067-4076 (1996) and by Bhattacharya, et al. in *J. Materials Science,* Vol. 32, pages 577-560 (1997).

Mixed Cr-Co oxides having a spinel structure are known (see e.g., Bracconi et al. in *Ann. Chim. Fr.*, Vol. 4, pages 331-338 (1979) and Hanck and Laitinen in *J. Inorg. Nucl. Chem.,* Volume 33, pages 63-73 (1971)).

$CrCoO_3$ is referenced as an interconnector material in a fuel cell assembly (see Chem. Abs. 118:9397). Various mixed metal oxides containing cobalt and chromium are also disclosed in Castiglioni, et al., *J. Solid State Chemistry,* Vol. 152, 526-532 (2000); Nowotny et al., *J. Am. Ceram. Soc.,* Vol. 65, pages 192-196 (1982); and Zhang et al., *Journal of Power Sources,* Vol. 83, pages 121-127 (1999).

Certain metal oxides are used as catalysts and/or catalyst precursors in the manufacture of fluorinated hydrocarbons. Chromium(III) oxide in particular is useful as it has been found that it may be fluorinated

by HF at elevated temperature to a give mixture of chromium fluoride and chromium oxyfluoride species which are active catalysts for conversion of C-Cl bonds to C-F bonds in the presence of HF. This conversion of C-Cl bonds to C-F bonds by the action of HF, known generally as halogen exchange, is a key step in many fluorocarbon manufacturing processes.

Chromium oxide compositions useful as catalyst precursors may be prepared in various ways or may take various forms. Chromium oxide suitable for vapor phase fluorination reactions may be prepared by reduction of Cr(VI) trioxide, by dehydration of Guignet's green, or by precipitation of Cr(III) salts with bases (see U. S. Patent No. 3,258,500). Another useful form of chromium oxide is hexagonal chromium oxide hydroxide with low alkali metal ion content as disclosed in U. S. Patent No. 3,978,145. Compounds such as MF_4 (M = Ti, Th, Ce), MF_3 (M = Al, Fe, Y), and MF_2 (M = Ca, Mg, Sr, Ba, Zn) have been added to hexagonal chromium oxide hydroxide to increase catalyst life as disclosed in U.S. Patent No. 3,992,325. A form of chromium oxide that is a precursor to a particularly active fluorination catalyst is that prepared by pyrolysis of ammonium dichromate as disclosed in U. S. Patent No. 5,036,036.

The addition of other compounds (e.g., other metal salts) to supported and/or unsupported chromium-based fluorination catalysts has been disclosed. Australian Patent Document No. AU-A-80340/94 discloses bulk or supported catalysts based on chromium oxide (or oxides of chromium) and at least one other catalytically active metal (e.g., Mg, V, Mn, Fe, Co, Ni, or Zn), in which the major part of the oxide(s) is in the crystalline state (and when the catalyst is a bulk catalyst, its specific surface, after activation with HF, is at least 8 m^2/g). The crystalline phases disclosed include Cr_2O_3, CrO_2, $NiCrO_3$, $NiCrO_4$, $NiCr_2O_4$, $MgCrO_4$, $ZnCr_2O_4$ and mixtures of these oxides. Australian Patent Document AU-A-29972/92 discloses a mass catalyst based on chromium and nickel oxides in which the Ni/Cr atomic ratio is between 0.05 and 5. U.S. Patent Application Publication No. US2001/0011061 A1 discloses chromia-based fluorination catalysts (optionally containing Mg, Zn, Co, and Ni) in which the chromia is at least partially crystalline. Fluorinated catalysts containing cobalt and chromium in combination (e.g. impregnated on a support) are among those disclosed in U.S. Patent No. 5,185,482. U.S. Patent No. 5,559,069 discloses homogeneously dispersed multiphase catalyst compositions characterized by dispersed phases of certain divalent metal

fluorides (certain fluorides of Mn, Co, Zn, Mg, and/or Cd) and certain trivalent metal fluorides (fluorides of Al, Ga, V, and /or Cr).

There remains a need for halogen exchange catalysts that can be used for processes such as the selective fluorination and chlorofluorination of saturated and unsaturated hydrocarbons, hydrochlorocarbons, hydrochlorofluorocarbons, and chlorofluorocarbons, the fluorination of unsaturated fluorocarbons, the isomerization and disproportionation of fluorinated organic compounds, the dehydrofluorination of hydrofluorocarbons, and the chlorodefluorination of fluorocarbons.

SUMMARY OF THE INVENTION

This invention provides a crystalline alpha-chromium oxide where from about 0.05 atom % to about 6 atom % of the chromium atoms in the alpha-chromium oxide lattice are replaced by trivalent cobalt (Co^{+3}) atoms, and a chromium-containing catalyst composition comprising as a chromium-containing component said crystalline cobalt-substituted alpha-chromium oxide.

This invention also provides a method for preparing a composition comprising said crystalline cobalt-substituted alpha-chromium oxide. The method comprises (a) co-precipitating a solid by adding ammonium hydroxide (aqueous ammonia) to an aqueous solution of a soluble cobalt salt and a soluble trivalent chromium salt that contains at least three moles of nitrate (i.e., NO_3^-) per mole of chromium (i.e., Cr^{3+}) in the solution and has a cobalt concentration of from about 0.05 mole % to about 6 mole % of the total concentration of cobalt and chromium in the solution; and after at least three moles of ammonium (i.e., NH_4^+) per mole of chromium (i.e., Cr^{3+}) in the solution has been added to the solution, (b) collecting the co-precipitated solid formed in (a); (c) drying the collected solid; and (d) calcining the dried solid.

This invention also provides a chromium-containing catalyst composition comprising a chromium-containing component prepared by treating said crystalline cobalt-substituted alpha-chromium oxide with a fluorinating agent (e.g., hydrogen fluoride).

This invention also provides a process for changing the fluorine distribution (i.e., content and/or arrangement) in a hydrocarbon or halogenated hydrocarbon in the presence of a catalyst. The process is characterized by using as the catalyst a composition comprising at least one chromium-containing component selected from the group consisting

of said crystalline cobalt-substituted alpha-chromium oxides and said treated cobalt-substituted alpha-chromium oxides.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 represents an energy dispersive spectroscopy spectrum for a sample of cobalt-substituted alpha-chromium oxide nominally containing 2 atom % cobalt.

Figure 2 represents an energy dispersive spectroscopy spectrum for a sample of alpha-chromium oxide without cobalt substitution.

Figure 3 represents an energy dispersive spectroscopy spectrum for a sample of cobalt chromium spinel.

Figure 4 represents a plot of the radial distribution function (i.e., the probability of finding an atom at a certain distance, r, from a central atom) associated with the local atomic structure around (a) a cobalt central atom in CoO, (b) a cobalt central atom in Co_3O_4, (c) a chromium central atom in Cr_2O_3, (d) cobalt in a sample of cobalt-substituted alpha-chromium oxide nominally containing 2 atom % cobalt and (e) cobalt in a sample of cobalt-substituted alpha-chromium oxide nominally containing 10 atom % cobalt.

DETAILED DESCRIPTION

New compositions of this invention comprise cobalt-substituted alpha-chromium oxide containing from about 0.05 atom % to about 6 atom % cobalt based on the total of the cobalt and chromium in the alpha-chromium oxide which retains the corundum structure. This invention includes a catalytic composition comprising said crystalline cobalt-substituted α-Cr_2O_3. The crystalline cobalt-substituted alpha-chromium oxides have the general formula α-$Co_xCr_{2-x}O_3$ where x = 0.001-0.12.

The compositions of the present invention may be prepared by the method described above using co-precipitation. In the typical co-precipitation technique, an aqueous solution of cobalt(II) or cobalt(III) salts and chromium(III) salts is prepared. The relative concentrations of cobalt and chromium(III) salts in the aqueous solution is dictated by the bulk mole percent cobalt relative to chromium desired in the final catalyst. The concentration of chromium(III) in the aqueous solution is typically in the range of from 0.3 to 3 molar (moles per liter) with 0.75-1.5 molar being a preferred concentration. Chromium(III) salts suitable for preparation of the aqueous solution are the nitrate, sulfate, acetate, formate, oxalate, phosphate, bromide, and chloride and various hydrated forms of these salts. Other chromium(III) salts that are useful for the preparation of the aqueous solutions include hexacoordinate complexes of the formula

$[CrL_{6-z}A_z]^{+3-z}$ where each L is a neutral (i.e., uncharged) ligand selected from the group consisting of H_2O, NH_3, C_1-C_4 primary, secondary, or tertiary organic amines, a C_1-C_4 alkyl nitriles, or pyridine, where each A is an anionic ligand selected from the group consisting of fluoride, chloride, bromide, iodide, hydroxide, nitrite, and nitrate, and where z has a value of from 0 to 3 inclusive. Included are neutral bidentate ligands such as ethylene diamine which are equivalent to two L in that they may occupy two coordination sites. Also included are anionic bidentate ligands such as C_1-C_4 carboxylate which may occupy two coordination sites. Also included are dianionic ligands such as sulfate which are equivalent to two A ligands and may occupy more than one coordination site.

Salts containing alkali metals such as chromium potassium sulfate are not preferred because the presence of alkali metals can hinder catalyst activity (see U. S. Patent 4,843,181). Chromium(VI) precursors, such as CrO_3, though not preferred, may be used but require reduction to Cr(III) with a compound such as ethanol before precipitation.

Chromium(III) nitrate, or its hydrated forms such as $[Cr(NO_3)_3(H_2O)_9]$, are the most preferred chromium(III) salt for preparation of said aqueous solution.

Cobalt(II) salts suitable for preparation of the aqueous solution are the nitrate, sulfate, formate, oxalate, bromide, and chloride and various hydrated forms of these salts. Salts containing alkali metals such as cobalt potassium bis(sulfate) are not preferred because the presence of alkali metals can hinder catalyst activity. Cobalt(II) nitrate hydrate (e.g., $[Co(NO_3)_2(H_2O)_6]$) is the most preferred cobalt(II) salt.

Cobalt(III) salts that are useful for the preparation of the aqueous solutions include hexacoordinate complexes of the formula $[CoL_{6-z}A_z]^{+3-z}$ where each L is a neutral (i.e., uncharged) ligand selected from the group consisting of H_2O, NH_3, C_1-C_4 primary, secondary, or tertiary organic amine, a C_1-C_4 alkyl nitrile, or pyridine, where each A is an anionic ligand selected from the group consisting of fluoride, chloride, bromide, iodide, hydroxide, nitrite, and nitrate, and where a has a value of from 0 to 3 inclusive. Included are neutral bidentate ligands such as ethylene diamine which are equivalent to two L in that they may occupy two coordination sites. Also included are anionic bidentate ligands such as C_1-C_4 carboxylate which may occupy two coordination sites. Also included are dianionic ligands such as sulfate which are equivalent to two A ligands and may occupy more than one coordination site. Preferred cobalt(III) starting

materials are hexammine salts (e.g., $[Co(NH_3)_6]^{+3}$ where the counter ion is chloride or nitrate. Hexaamminecobalt(III) chloride (e.g., $[Co(NH_3)_6]Cl_3$]) is the most preferred cobalt(III) salt.

The aqueous solution of the cobalt salts and chromium(III) salts may then be evaporated either under vacuum or at elevated temperature to give a solid which is then calcined.

Preferably, however, the aqueous solution of the cobalt salts and chromium(III) salts is then treated with a base such as ammonium hydroxide (aqueous ammonia) to precipitate cobalt and chromium as the hydroxides. Bases containing alkali metals such as sodium or potassium hydroxide or the carbonates may be used but are not preferred. The addition of ammonium hydroxide to the aqueous solution of cobalt and chromium(III) salts is typically carried out gradually over a period of 1 to 12 hours. The pH of the solution is monitored during the addition of base. The final pH is typically in the range of 6.0 to 11.0, preferably from about 7.5 to about 9.0, and most preferably from about 8.0 to 8.7. The precipitation of the cobalt hydroxide/chromium hydroxide mixture is typically carried out at a temperature of about 15°C to about 60°C, preferably from about 20°C to about 40°C. After the ammonium hydroxide is added, the mixture is typically stirred for up to 24 hours.

Of note are preparations where excess ammonium nitrate (i.e., more than three moles of ammonium nitrate per mole of chromium) is present in the aqueous solution. For example, in addition to the ammonium nitrate already present from reaction of ammonium hydroxide with chromium nitrate, from about 0.1 mole to about 7.0 moles of additional ammonium nitrate per mole of chromium may be added to the solution before, during, or after the co-precipitation of the compositions. Surprisingly, we have found that addition of excess ammonium nitrate to the precipitated mixture of cobalt and chromium hydroxides prior to the dehydration step may be used to decrease the particle size of the α-$Co_xCr_{2-x}O_3$ phase which in turn increases the surface area of that phase and the activity of the catalyst (see PREPARATION EXAMPLES 15, 17, and 18 and EXAMPLES 20, 21, 30, and 31).

After the ammonium nitrate is added to the mixture, it is preferably stirred for about 0.5 to ten hours (preferably for about one to five hours) at a temperature of from about 20°C to about 60°C. The mixture is then dried and calcined as indicated below.

Other agents that serve this purpose include aqueous hydrogen peroxide (1% to 30% solutions), ozone, peroxy acids such as peroxyacetic acid, and ammonium persulfate. Agents such as halogens may be used but are not preferred. Agents containing alkali metals such as potassium persulfate or sodium perborate may also be used, but are not preferred.

After the precipitation of the mixture of cobalt and chromium hydroxides is complete, and the ammonium nitrate or other agents added if desired, the mixture is dried by evaporation.

Optionally, the precipitated cobalt and chromium hydroxide mixture may be collected and, if desired, washed with deionized water before drying. This may influence the activity of the catalyst (see Examples 32 and 33).

After the cobalt and chromium hydroxide mixture has been dried, the nitrate salts are then decomposed by heating the solid from about 250°C to about 350°C. The resulting solid is then calcined at temperature of from about 375°C to about 1000°C, preferably from about 400°C to about 600°C. The calcination temperature can influence the activity of the catalysts and, in turn, the product distribution when the catalysts are used to change the fluorine distribution in hydrocarbons and halogenated hydrocarbons (see Examples 34 and 35). Lower calcination temperatures may result in the presence of some residual nitrate impurities.

The calcination is preferably carried out in the presence of oxygen, most preferably in the presence of air.

The metal oxide compositions of this invention may be characterized by well-established analytical techniques including X-Ray absorption spectroscopy (XAS), X-ray powder diffraction (XRD), transmission electron microscopy (TEM), and energy dispersive spectroscopy (EDS). EDS is an analytical tool available in conjunction with scanning or analytical TEM.

After calcination, the resulting cobalt-substituted crystallites are not visually distinguishable from α-Cr_2O_3 by TEM. Furthermore, X-ray and electron diffraction studies are entirely consistent with the α-Cr_2O_3 structure with some lattice contraction proportional to the amount of Co(III) substituted for Cr(III) in the structure. The compositions are therefore concluded to have the general formula α-$Co_xCr_{2-x}O_3$ where x = 0.001-0.12.

The presence of cobalt in the various cobalt/chromium compositions of this invention is clearly indicated by elemental analysis

using EDS. Figure 1 shows the EDS spectrum of a sample of a cobalt-substituted α-Cr_2O_3 nominally containing 2 atom % Co. For comparison, Figure 2 shows the EDS spectrum of α-Cr_2O_3 without cobalt substitution and Figure 3 shows the EDS spectrum of commercially available $CoCr_2O_4$, a cobalt chromium spinel. In each of these three figures X-ray intensity, I, representing thousands of counts is plotted against energy level, E, representing thousands of electron volts (keV). Peaks in each plot correlate with the presence of certain elements. The presence of cobalt is clearly indicated in the EDS spectrum in Figure 1 while the cobalt peaks are absent in Figure 2. At higher loadings of cobalt (e.g., compositions having a bulk composition of cobalt greater than about 6 atom % cobalt based on the total metal content), a second spinel-like phase with a nominal composition $(Cr_{0.5}Co_{0.5})_3O_4$ and with a crystallite size in the range of 10 nm can be easily identified by TEM and EDS. The relative heights of 2:1 for the K_α peaks of Cr (atomic mass 52) and Co (atomic mass 59), respectively, in Figure 3 indicate that the EDS data are valid on a quantitative basis.

XAS and XRD data were obtained for compositions that were nominally 100% Cr (no cobalt added), Cr98%/Co2%, Cr95%/Co5%, and Cr90%/Co10%. XAS and XRD analysis clearly show that cobalt is substituted into α-Cr_2O_3. XRD results for Cr98%Co2% are shown in Table 1. Diffraction peaks having d-spacings of 3.1368, 1.9211, 1.3581, 1.2464, and 1.1088 are due to a silicon internal standard added to the sample for calibration of the diffractometer. All other diffraction peaks can be indexed to the α-Cr_2O_3 structure with a slightly reduced unit cell volume.

TABLE 1

XRD Results for a Co-Substituted alpha-Cr_2O_3 Composition that is Nominally 98 atom % Cr/2 atom % Co

d (Angstroms)	Height	FWHM [a]
3.6263	134	0.627
3.1368	2539	0.135
2.6635	288	0.607
2.4656	668	0.448
2.2550	53	0.312
2.1661	292	0.450
2.0430	16	0.469
1.9211	1842	0.136

1.8105	128	0.634
1.6654	707	0.510
1.6382	1076	0.223
1.5772	37	0.202
1.4644	98	0.533
1.4260	289	0.579
1.3581	274	0.195
1.2907	92	0.762
1.2464	460	0.159
1.2352	55	0.566
1.2055	44	0.516
1.1486	40	0.283
1.1238	38	0.362
1.1088	689	0.162
1.1059	272	0.215

a. FWHM means full width at half maximum.

If Co substitutes for Cr in the α-Cr_2O_3 phase, it is expected to be in octahedral coordination (N Co-O = 6) and in the 3+ oxidation state. XAS results from the Cr-K edge of the samples indicate that all Cr is present as Cr^{3+} and is octahedrally coordinated. If the cobalt is present in the spinel-like phase observed by electron microscopy, some of these atoms will have tetrahedral coordination and be present in the +2 oxidation state.

Figure 4 shows the radial distribution function (RDF) for five materials. The radial distribution function represents the probability of finding an atom at a certain distance, r, from a central atom. These probabilities are weighted by factors that depend on the type of atom. Thus an RDF is a representation of local atomic structure around the central atom. An RDF is obtained by Fourier transform of the extended x-ray absorption fine structure (EXAFS) data, and may be represented by a plot of the dimensionless Fourier transform magnitude, F, versus the pair separation distance in angstroms. In simplified terms, one might view a peak in an RDF plot as indicative of a distance at which there is a coordination sphere around the central atom. A small difference is expected between the actual separation distance and the "r" shown in a plot when no correction is made to account for the phase shift on backscattering of excited electrons. In Figure 4, F is plotted against the pair separation distance, r (shown in angstroms, uncorrected for phase shift) for each of the five materials. Included in Figure 4 are curve A representing the local structure around cobalt in CoO, curve B

representing the local structure around cobalt in Co_3O_4, curve C representing the local structure around chromium in α-Cr_2O_3. Also included in Figure 4 is curve D representing the local structure around cobalt in the cobalt-substituted alpha-chromium oxide with a nominal composition of 98% chromium and 2% cobalt, and curve E representing the local structure around cobalt in the cobalt-substituted alpha-chromium oxide with a nominal composition of 90% chromium and 10% cobalt. No spinel phase was detected by electron microscopy in this sample, so all the Co is considered to be associated with the α-Cr_2O_3 phase, either as a separate cobalt oxide coating, or as a substitute for Cr in the α-Cr_2O_3 lattice. The curve in Figure 4 representing the local structure around cobalt in the cobalt-substituted alpha-chromium oxide with a nominal composition of 98% chromium and 2% cobalt, indicates that the local atomic structure around Co in this sample bears no resemblance to that of expected common cobalt oxide phases, but is very similar to that of Cr in the α-Cr_2O_3 phase.

Table 2 shows average first near neighbor coordination numbers (N Co-O) and average Co oxidation states obtained from XAS analysis of the Co K edge absorption spectra as well as unit cell volumes for the α-Cr_2O_3 -like phase obtained by XRD.

TABLE 2

Characterization of Metal-Substituted alpha-Chromium(III) Oxide

Composition	Cr/Co atom %	Average N (Co-O)	Average Co Oxid. State	UnitCell Volume (nm^3)
Cr100%	100/0			0.284839
Cr98%Co2%	98/2	6.01	2.940	0.284614
Cr95%Co5%	95/5	5.67	2.840	0.284268
Cr90%Co10%	90/10	5.46	2.634	0.284177

The reduction in unit cell volume on introduction of Co can be understood by consideration of ionic radii. If Co^{+3} substitute into the octahedral environment of Cr^{+3} in α-Cr_2O_3, they will adopt a low spin configuration as discussed by Cotton in chapter 8 of *Chemical Applications of Group Theory*, 3rd ed. (New York, Wiley, 1990). Using ionic radii of high spin Cr^{+3} (62 pm), low spin Co^{+3} (53 pm), and O^{-2} (137 pm) as given by Shannon and Prewitt in *Acta Crystallographica*, Volume B25, pages 925 to 945 (1969), the unit cell volume contraction may be related to the amount

of low spin Co^{+3} substituted for high spin Cr^{+3} in the α-Cr_2O_3 lattice. These relationships are summarized in Table 3 which shows the amount of cobalt actually substituted into the α-Cr_2O_3 phase for the four Co-substituted compositions based on coordination numbers, oxidation states, and unit cell volumes. The data in Table 3 are in good agreement and suggest a solubility limit of cobalt in the α-Cr_2O_3 phase of about 6 atom %. Further indication of the cobalt solubility limitation for bulk cobalt concentrations above 6 atom % is provided by the curve in Figure 4 which represents the local structure around cobalt in the cobalt-substituted alpha-chromium oxide with a nominal composition of 90% chromium and 10% cobalt. This curve suggests that some of the cobalt is present as Co_3O_4.

TABLE 3

Amount of Cobalt Substituted into α-Cr_2O_3 Lattice for Various Compositions

	Atom % Co Substituted into alpha-Cr_2O_3 Lattice		
Composition	Based on N (Co-O)	Based on Co Oxid'n State	Based on Unit Cell Vol.
Cr98%/Co2%	2.00 (0.15)	1.82 (0.03)	1.72 (0.4)
Cr95%/Co5%	3.75 (0.38)	3.80 (0.08)	4.37 (0.4)
Cr90%/Co10%	5.94 (0.75)	4.51 (0.15)	5.06 (0.4)

Other phases such as chromium-cobalt spinel phases may be present in the chromium oxide compositions of the present invention. The presence of these phases having an overall stoichiometry of $(Co_{0.5}Cr_{0.5})_3O_4$ was detected by EDS and TEM. These phases were normally minor relative to the α-Cr_2O_3-like phase and usually had smaller particle sizes.

The surface area of the chromium oxide compositions of the present invention is typically in the range of about 1 to 100 m^2/gram. The α-$Co_xCr_{2-x}O_3$ phase present in the compositions prepared by the process of this invention is typically made up of crystallites having a particle sizes varying from about 20 to about 400 nm, typically from about 40 to about 250 nm. Included in this invention are microcrystalline materials with particle sizes smaller than 20 nm.

The calcined chromium oxide compositions of the present invention may be formed into various shapes such as pellets, granules, and extrudates for use in packing reactors. It may also be used in powder form.

The cobalt content of the chromium oxide compositions of the present invention effects the activity of the catalyst obtained after fluorinating the mixed metal oxide. For example, in the chlorofluorination of CCl_2=$CClCF_3$ to $CF_3CClFCF_3$, the activity of the fluorinated metal oxide catalysts containing cobalt and chromium for formation of $CF_3CClFCF_3$ is improved for those compositions having 2-5 atom % cobalt in the catalyst relative to a chrome catalyst containing no cobalt (see TABLE 4). Furthermore, in accord with the teachings of this invention the activity of a composition containing a given ratio of cobalt to chromium may be enhanced by treating the initial solution of cobalt(II) and chromium(III) nitrates with an agent such as ammonium nitrate prior to dehydration and calcination.

TABLE 4

Activity of Fluorinated Cobalt/Chromium Oxides for Chlorofluorination of CCl_2=$CClCF_3$ to $CF_3CClFCF_3$ [a.]

Cr/Co Ratio	Calcination Temperature	% $CF_3CClFCF_3$ in Product at 400°C
100/0	400°C	24.1
99/1	400°C	47.4
98/2	400°C	46.6
98/2	550°C	36.7
97/3	400°C, washed	31.7
95/5	400°C, excess NH_4NO_3	27.6 [b.]

a. Catalysts were prepared by co-precipitation technique using ammonia. Molar feed ratios of HF, 1213xa, and Cl_2 = 30:1:2.

b. Reactor temperature 350°C.

Cobalt chromium spinel is not considered an effective catalysts for fluorination or chlorofluorination reactions (see COMPARATIVE EXAMPLE 26).

The compositions of this invention may further comprise one or more additives in the form of metal compounds that alter the selectivity or activity of the crystalline cobalt-substituted alpha-chromium oxides or the fluorinated metal oxide catalysts containing cobalt and chromium. Suitable additives may be selected from the group consisting of fluorides, oxides, or oxyfluoride compounds of Mg, Ca, Sc, Y, La, Ti, Zr, Hf, V, Nb, Ta, Mo, W, Mn, Re, Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Ce, and Zn.

The total content of the additive(s) in the compositions of the present invention may be from about 0.05 atom % to about 15 atom % based on the total metal content of the compositions. The additives may be incorporated into the compositions of the present invention by standard procedures such as by impregnation.

Typically, the calcined compositions will be pre-treated with a fluorinating agent prior to use as catalysts for changing the fluorine distribution of hydrocarbons and/or halogenated hydrocarbon compounds. Typically this fluorinating agent is HF though other materials may be used such sulfur tetrafluoride, carbonyl fluoride, and fluorinated hydrocarbon compounds such as trichlorofluoromethane, dichlorodifluoromethane, chlorodifluoromethane, trifluoromethane, or 1,1,2-trichlorotrifluoroethane. This pretreatment can be accomplished, for example, by placing the catalyst in a suitable container which can be the reactor to be used to perform the process in the instant invention, and thereafter, passing HF over the dried, calcined catalyst so as to partially saturate the catalyst with HF. This is conveniently carried out by passing HF over the catalyst for a period of time, for example, about 0.1 to about 10 hours at a temperature of, for example, about 200°C to about 450°C. Nevertheless, this pre-treatment is not essential.

As noted above catalysts provided in accordance with this invention may be used for changing the fluorine distribution in hydrocarbons and/or halogenated hydrocarbons. The fluorine distribution in a hydrocarbon or a halogenated hydrocarbon may be changed by increasing the fluorine content of the hydrocarbon or the halogenated hydrocarbon. The fluorine distribution of a halogenated hydrocarbon may also be changed by decreasing the fluorine content of the halogenated hydrocarbon and/or rearranging the placement of fluorine atoms on the carbon atoms of the halogenated hydrocarbon. Of note are processes where the fluorine distribution in halogenated hydrocarbons containing from one to twelve carbon atoms is changed, particularly processes where the fluorine

distribution in halogenated hydrocarbons containing from one to six carbon atoms is changed. Also of note are processes where the fluorine content of hydrocarbons containing from one to twelve carbon atoms is increased, particularly processes where the fluorine content in hydrocarbons containing one to six carbon atoms is increased. Processes for changing the fluorine distribution in halogenated hydrocarbons include fluorination, chlorofluorination, isomerization, disproportionation, dehydrofluorination and chlorodefluorination. The processes of this invention are characterized by using as the catalyst a composition comprising at least one chromium-containing component selected from the group consisting of the crystalline cobalt-substituted alpha-chromium oxide described above and said cobalt-substituted alpha-chromium oxide which has been treated with a fluorinating agent. Typical of saturated halogenated hydrocarbons suitable for fluorination, chlorofluorination, isomerization, disproportionation, dehydrofluorination and chlorodefluorination processes are those which have the formula $C_nH_aBr_bCl_cF_d$, wherein n is an integer from 1 to 6, a is an integer from 0 to 12, b is an integer from 0 to 4, c is an integer from 0 to 13, d is an integer from 0 to 13, the sum of b, c and d is at least 1 and the sum of a, b, c, and d is equal to 2n + 2, provided that n is at least 2 for isomerization, disproportionation and dehydrofluorination processes, a is at least one for dehydrofluorination processes, b is 0 for chlorodefluorination processes, b + c is at least 1 for fluorination processes and is 0 for dehydrofluorination processes, a + b + c is at least 1 for fluorination, chlorofluorination, isomerization, disproportionation and dehydrofluorination processes and d is at least 1 for isomerization, disproportionation, dehydrofluorination and chlorodefluorination processes. Typical of unsaturated halogenated hydrocarbons suitable for fluorination, chlorofluorination, isomerization, disproportiopnation, and chlorodefluorination processes are those which have the formula $C_pH_eBr_fCl_gF_h$, wherein p is an integer from 2 to 6, e is an integer from 0 to 10, f is an integer from 0 to 2, g is an integer from 0 to 12, h is an integer from 0 to 11, the sum of f, g and h is at least 1 and the sum of e, f, g, and h is equal to 2p, provided that f is 0 for chlorodefluorination processes, e + f + g is at least 1 for isomerization and disproportionation processes and h is at least 1 for isomerization, disproportionation and chlorodefluorination processes. Typical of saturated hydrocarbons suitable for chlorofluorination are those which have the formula C_qH_r where q is an integer from 1 to 6 and r is 2q + 2. Typical of unsaturated hydrocarbons

suitable for fluorination and chlorofluorination are those which have the formula C_iH_j where i is an integer from 2 to 6 and j is 2i.

Fluorination

Included in this invention is a process for increasing the fluorine content of a halogenated hydrocarbon compound or an unsaturated hydrocarbon compound by reacting said compound with hydrogen fluoride in the vapor phase in the presence of a catalyst composition comprising at least one chromium-containing component selected from the group consisting of the crystalline cobalt-substituted alpha-chromium oxide described above and said cobalt-substituted alpha-chromium oxide which has been treated with a fluorinating agent. The catalyst composition may optionally contain additional components such as additives to alter the activity and selectivity of the catalyst.

Halogenated hydrocarbon compounds suitable as starting materials for the fluorination process of this invention may be saturated or unsaturated. Saturated halogenated hydrocarbon compounds suitable for the fluorination processes of this invention include those of the general formula $C_nH_aBr_bCl_cF_d$, wherein n is an integer from 1 to 6, a is an integer from 0 to 12, b is an integer from 0 to 4, c is an integer from 0 to 13, d is an integer from 0 to 13, and the sum of a, b, c, and d is equal to 2n + 2, provided that b + c is at least 1. Unsaturated halogenated hydrocarbon compounds suitable for the fluorination processes of this invention include those of the general formula $C_pH_eBr_fCl_gF_h$, wherein p is an integer from 2 to 6, e is an integer from 0 to 10, f is an integer from 0 to 2, g is an integer from 0 to 12, h is an integer from 0 to 11, the sum of f, g and h is at least 1 and the sum of e, f, g, and h is equal to 2p. Unsaturated hydrocarbons suitable for fluorination are those which have the formula CiHj where i is an integer from 2 to 6 and j is 2i. The fluorine content of saturated compounds of the formula $C_nH_aBr_bCl_cF_d$, unsaturated compounds of the formula $C_pH_eBr_fCl_gF_h$ and/or unsaturated compounds of the formula C_iH_j may be increased by reacting said compounds with HF in the vapor phase in the presence of a catalyst composition comprising at least one chromium-containing component selected from the group consisting of the crystalline cobalt-substituted alpha-chromium oxide described above and said cobalt-substituted alpha- chromium oxide which has been treated with a fluorinating agent. Such a process is referred to herein as a vapor phase fluorination reaction.

The vapor phase fluorination reactions are typically conducted at temperatures of from about 150°C to 500°C. For saturated compounds the fluorination is preferably carried out from about 175°C to 400°C and more preferably from about 200°C to about 350°C. For unsaturated compounds the fluorination is preferably carried out from about 150°C to 350°C and more preferably from about 175°C to about 300°C.

The vapor phase fluorination reactions are typically conducted at atmospheric and superatmospheric pressures. For reasons of convenience in downstream separations processes (e.g., distillation), pressures of up to about 30 atmospheres may be employed.

The vapor phase fluorination reactions are typically conducted in a tubular reactor. The reactor and its associated feed lines, effluent lines, and associated units should be constructed of materials resistant to hydrogen fluoride and hydrogen chloride. Typical materials of construction, well-known to the fluorination art, include stainless steels, in particular of the austenitic type, the well-known high nickel alloys, such as Monel® nickel-copper alloys, Hastelloy® nickel-based alloys and, Inconel® nickel-chromium alloys, and copper-clad steel.

The contact time in the reactor is typically from about 1 to about 120 seconds and preferably from about 5 to about 60 seconds.

The amount of HF reacted with the unsaturated hydrocarbons or halogenated hydrocarbon compounds should be at least a stoichiometric amount. The stoichiometric amount is based on the number of Br and/or Cl substituents to be replaced by F in addition to one mole of HF to saturate the carbon-carbon double bond if present. Typically, the molar ratio of HF to the said compounds of the formulas $C_nH_aBr_bCl_cF_d$, $C_pH_eBr_fCl_gF_h$, and C_iH_j can range from about 0.5:1 to about 100:1, preferably from about 2:1 to about 50:1, and more preferably from about 3:1 to about 20:1. In general, with a given catalyst composition, the higher the temperature and the longer the contact time, the greater is the conversion to fluorinated products. The above variables can be balanced, one against the other, so that the formation of higher fluorine substituted products is maximized.

Examples of saturated compounds of the formula $C_nH_aBr_bCl_cF_d$ which may be reacted with HF in the presence of the catalyst of this invention include CH_2Cl_2, CH_2Br_2, $CHCl_3$, CCl_4, C_2Cl_6, C_2BrCl_5, C_2Cl_5F, $C_2Cl_4F_2$, $C_2Cl_3F_3$, $C_2Cl_2F_4$, C_2ClF_5, C_2HCl_5, C_2HCl_4F, $C_2HCl_3F_2$, $C_2HCl_2F_3$, C_2HClF_4, C_2HBrF_4, $C_2H_2Cl_4$, $C_2H_2Cl_3F$, $C_2H_2Cl_2F_2$,

$C_2H_2ClF_3$, $C_2H_3Cl_3$, $C_2H_3Cl_2F$, $C_2H_3ClF_2$, $C_2H_4Cl_2$, C_2H_4ClF, $C_3Cl_6F_2$, $C_3Cl_5F_3$, $C_3Cl_4F_4$, $C_3Cl_3F_5$, C_3HCl_7, C_3HCl_6F, $C_3HCl_5F_2$, $C_3HCl_4F_3$, $C_3HCl_3F_4$, $C_3HCl_2F_5$, $C_3H_2Cl_6$, $C_3H_2BrCl_5$, $C_3H_2Cl_5F$, $C_3H_2Cl_4F_2$, $C_3H_2Cl_3F_3$, $C_3H_2Cl_2F_4$, $C_3H_2ClF_5$, $C_3H_3Cl_5$, $C_3H_3Cl_4F$, $C_3H_3Cl_3F_2$, $C_3H_3Cl_2F_3$, $C_3H_3ClF_4$, $C_3H_4Cl_4$, $C_4Cl_4Cl_4$, $C_4Cl_4Cl_6$, $C_4H_5Cl_5$, $C_4H_5Cl_4F$, and $C_5H_4Cl_8$.

Specific examples of fluorination reactions of saturated halogenated hydrocarbon compounds which may be carried out under the conditions described above using the catalysts of this invention include the conversion of CH_2Cl_2 to CH_2F_2, the conversion of $CHCl_3$ to a mixture of $CHCl_2F$, $CHClF_2$, and CHF_3, the conversion of CH_3CHCl_2 to a mixture of CH_3CHClF and CH_3CHF_2, the conversion of CH_2ClCH_2Cl to a mixture of CH_3CHClF and CH_3CHF_2, the conversion of CH_3CCl_3 to a mixture of CH_3CCl_2F, CH_3CClF_2, and CH_3CF_3, the conversion of CH_2ClCF_3 to CH_2FCF_3, the conversion of $CHCl_2CF_3$ to a mixture of $CHClFCF_3$ and CHF_2CF_3, the conversion of $CHClFCF_3$ to CHF_2CF_3, the conversion of $CHBrFCF_3$ to CHF_2CF_3, the conversion of $CCl_3CF_2CCl_3$ to a mixture of $CCl_2FCF_2CClF_2$ and $CClF_2CF_2CClF_2$, the conversion of $CCl_3CH_2CCl_3$ to $CF_3CH_2CF_3$, the conversion of $CCl_3CH_2CHCl_2$ to a mixture of $CF_3CH_2CHF_2$, $CF_3CH{=}CHCl$, and $CF_3CH{=}CHF$, the conversion of $CF_3CCl_2CClF_2$ to a mixture of $CF_3CCl_2CF_3$, and CF_3ClFCF_3, the conversion of $CF_3CCl_2CF_3$ to CF_3ClFCF_3, and the conversion of a mixture comprising $CF_3CF_2CHCl_2$ and $CClF_2CF_2CHClF$ to a mixture of CF_3CF_2CHClF and $CF_3CF_2CHF_2$.

Examples of unsaturated compounds of the formula $C_pH_eBr_fCl_gF_h$ and C_iH_j which may be reacted with HF in the presence of the catalysts of this invention include C_2Cl_4, C_2BrCl_3, C_2Cl_3F, $C_2Cl_2F_2$, C_2ClF_3, C_2F_4, C_2HCl_3, C_2HBrCl_2, C_2HCl_2F, C_2HClF_2, C_2HF_3, $C_2H_2Cl_2$, C_2H_2ClF, $C_2H_2F_2$, C_2H_3Cl, C_2H_3F, C_2H_4, C_3H_6, C_3H_5Cl, $C_3H_4Cl_2$, $C_3H_3Cl_3$, $C_3H_2Cl_4$, C_3HCl_5, C_3Cl_6, C_3Cl_5F, $C_3Cl_4F_2$, $C_3Cl_3F_3$, $C_3Cl_2F_4$, C_3ClF_5, C_3HF_5, $C_3H_2F_4$, C_3F_6, C_4Cl_8, $C_4Cl_2F_6$, C_4ClF_7, $C_4H_2F_6$, and C_4HClF_6.

Specific examples of fluorination reactions of unsaturated halogenated hydrocarbon compounds which may be carried out using the catalysts of this invention include the conversion of $CHCl{=}CCl_2$ to a mixture of CH_2ClCF_3 and CH_2FCF_3, the conversion of $CCl_2{=}CCl_2$ to a mixture of $CHCl_2CF_3$, $CHClFCF_3$, and CHF_2CF_3, the conversion of $CCl_2{=}CH_2$ to a mixture of CH_3CCl_2F, CH_3CClF_2, and CH_3CF_3, the conversion of $CH_2{=}CHCl$ to a mixture of CH_3CHClF and CH_3CHF_2, the

conversion of $CF_2=CH_2$ to CH_3CF_3, the conversion of $CCl_2=CClCF_3$ to a mixture of $CF_3CHClCClF_2$, $CF_3CHClCF_3$, and/or $CF_3CCl=CF_2$, the conversion of $CF_3CF=CF_2$ to CF_3CHFCF_3, the conversion of $CF_3CH=CF_2$ to $CF_3CH_2CF_3$, and the conversion of $CF_3CH=CHF$ to $CF_3CH_2CHF_2$.

Further information on the production of pentafluoroethane is provided in U.S. Patent Application _____[CL2109 US PRV] filed concurrently herewith, and hereby incorporated by reference herein in its entirety.

Of note is a catalytic process for producing 1,1,1,2,2-pentafluoroethane (i.e., CHF_2CF_3 or HFC-125) by the fluorination of a haloethane of the formula CHZ_2CZ_3 where each Z is selected from the group consisting of F, Cl, and Br provided that no more than four of the Z are F. Preferred haloethanes of the formula CHZ_2CZ_3 include 2,2-dichloro-1,1,1-trifluoroethane (HCFC-123) and 1,2,2-trichloro-1,1-difluoroethane (HCFC-122). HFC-125 is produced by reacting the CHZ_2CZ_3 compounds with HF in the vapor phase in the presence of the catalysts of this invention. The reaction of the above pentahaloethanes with HF in the presence of the catalyst of the instant invention is preferably conducted at about 150°C to about 400°C, more preferably from about 200°C to about 380°C. The amount of HF fed to the reactor should be at least a stoichiometric amount based on the number of Cl or Br substituents in the CHZ_2CZ_3 starting material(s). In the case of fluorination of HCFC-123, the stoichiometric ratio of HF to HCFC-123 is 2:1. Preferred ratios of HF to CHZ_2CZ_3 starting material(s) are typically in the range of about the stoichiometric ratio to about 20:1. Preferred contact times are from 1 to 60 seconds. Oxygen in the form of air or co-fed with an inert diluent such as nitrogen, helium, or argon may be added along with the reactants or as a separate catalyst treatment, if desired.

Also of note is a catalytic process for producing 2-chloro-1,1,1,3,3,3-hexafluoropropane (i.e., $CF_3CHClCF_3$ or HCFC-226da) by the fluorination of a hexahalopropene of the formula $C_3Cl_{6-x}F_x$, wherein x equals 0 to 5. Preferred hexahalopropenes of the formula $C_3Cl_{6-x}F_x$ include 1,2,2-trichloro-3,3,3-trifluoro-1-propene (i.e., $CCl_2=CClCF_3$ or CFC-1213xa) and hexachloropropene (i.e., $CCl_2=CClCCl_3$). HCFC-226da is produced by reacting the above unsaturated compounds with HF in the vapor phase in the presence of the catalysts of this invention at temperatures from about 150°C to about 400°C, preferably about 200°C to about 350°C.

The amount of HF fed to the reactor should be at least a stoichiometric amount based on the number of Cl substituents in the $C_3Cl_{6-x}F_x$ starting material(s). In the case of fluorination of CFC-1213xa, the stoichiometric ratio of HF to CFC-1213xa is 3:1. Preferred ratios of HF to $C_3Cl_{6-x}F_x$ starting material(s) are typically in the range of about the stoichiometric ratio to about 25:1. Preferred contact times are from 1 to 60 seconds.

Mixtures of saturated halogenated hydrocarbon compounds or mixtures of unsaturated hydrocarbons and/or halogenated hydrocarbon compounds may also be used in the vapor phase fluorination reactions as well as mixtures comprising both unsaturated hydrocarbons and halogenated hydrocarbon compounds. Specific examples of mixtures of saturated halogenated hydrocarbon compounds and mixtures of unsaturated hydrocarbons and unsaturated halogenated hydrocarbon compounds that may be subjected to vapor phase fluorination using the catalysts of this invention include a mixture of CH_2Cl_2 and $CCl_2=CCl_2$, a mixture of CCl_2FCClF_2 and CCl_3CF_3, a mixture of $CCl_2=CCl_2$ and $CCl_2=CClCCl_3$, a mixture of $CH_2=CHCH_3$ and $CH_2=CClCH_3$, a mixture of CH_2Cl_2 and CH_3CCl_3, a mixture of CHF_2CClF_2 and $CHClFCF_3$, a mixture of $CHCl_2CCl_2CH_2Cl$ and $CCl_3CHClCH_2Cl$, a mixture of $CHCl_2CH_2CCl_3$ and $CCl_3CHClCH_2Cl$, a mixture of $CHCl_2CHClCCl_3$, $CCl_3CH_2CCl_3$, and $CCl_3CCl_2CH_2Cl$, a mixture of $CHCl_2CH_2CCl_3$ and $CCl_3CH_2CCl_3$, a mixture of and $CF_3CH_2CCl_2F$ and $CF_3CH=CCl_2$, and a mixture of $CF_3CH=CHCl$ and $CF_3CH=CCl_2$.

Chlorofluorination

Included in this invention is a process for increasing the fluorine content of a halogenated hydrocarbon compound or a hydrocarbon compound by reacting said compound with hydrogen fluoride (HF) and chlorine (Cl_2) in the vapor phase in the presence of a catalyst composition comprising at least one chromium-containing component selected from the group consisting of the crystalline cobalt-substituted alpha-chromium oxide described above and said cobalt-substituted alpha-chromium oxide which has been treated with a fluorinating agent. The catalyst composition may optionally contain additional components such as another catalytically effective metal.

Halogenated hydrocarbon compounds suitable as starting materials for the chlorofluorination process of this invention may be saturated or unsaturated. Saturated halogenated hydrocarbon compounds suitable for

the chlorofluorination processes of this invention include those of the general formula $C_nH_aBr_bCl_cF_d$, wherein n is an integer from 1 to 6, a is an integer from 0 to 12, b is an integer from 0 to 4, c is an integer from 0 to 13, d is an integer from 0 to 13, the sum of b, c and d is at least 1 and the sum of a, b, c, and d is equal to 2n + 2, provided that a + b + c is at least 1. Preferred chlorofluorination processes include those involving said saturated starting materials where a is at least 1. Saturated hydrocarbon compounds suitable for chlorofluorination are those which have the formula C_qH_r where q is an integer from 1 to 6 and r is 2q + 2. Unsaturated halogenated hydrocarbon compounds suitable for the chlorofluorination processes of this invention include those of the general formula $C_pH_eBr_fCl_gF_h$, wherein p is an integer from 2 to 6, e is an integer from 0 to 10, f is an integer from 0 to 2, g is an integer from 0 to 12, h is an integer from 0 to 11, the sum of f, g and h is at least 1 and the sum of e, f, g, and h is equal to 2p. Unsaturated hydrocarbon compounds suitable for fluorination are those which have the formula C_iH_j where i is an integer from 2 to 6 and j is 2i. The fluorine content of saturated compounds of the formula $C_nH_aBr_bCl_cF_d$ and C_qH_r and/or unsaturated compounds of the formula $C_pH_eBr_fCl_gF_h$ and C_iH_j may be increased by reacting said compounds with HF and Cl_2 in the vapor phase in the presence of a catalyst composition comprising at least one chromium-containing component selected from the group consisting of the crystalline cobalt-substituted alpha-chromium oxide described above and said cobalt-substituted alpha-chromium oxide which has been treated with a fluorinating agent. Such a process is referred to herein as a vapor phase chlorofluorination reaction.

The conditions of the vapor phase chlorofluorination reactions are similar to those described above for vapor phase fluorination reactions in terms of the temperature ranges, contact times, pressures, and mole ratios of HF to the halogenated hydrocarbon compounds. The amount of chlorine (Cl_2) fed to the reactor is based on whether the halogenated hydrocarbon compounds fed to the reactor is unsaturated and the number of hydrogens in $C_nH_aBr_bCl_cF_d$, C_qH_r, $C_pH_eBr_fCl_gF_h$, and C_iH_j that are to be replaced by chlorine and fluorine. One mole of Cl_2 is required to saturate a carbon-carbon double bond and a mole of Cl_2 is required for every hydrogen to be replaced by chlorine or fluorine. A slight excess of chlorine over the stoichiometric amount may be necessary for practical reasons, but large excesses of chlorine will result in complete chlorofluorination of

the products. The ratio of Cl_2 to halogenated carbon compound is typically from about 1:1 to about 10:1.

Specific examples of vapor phase chlorofluorination reactions of saturated halogenated hydrocarbon compounds of the general formula $C_nH_aBr_bCl_cF_d$ and saturated hydrocarbon compounds of the general formula C_qH_r which may be carried out using the catalysts of this invention include the conversion of C_2H_6 to a mixture containing CH_2ClCF_3, the conversion of CH_2ClCF_3 to a mixture of $CHClFCF_3$ and CHF_2CF_3, the conversion of $CCl_3CH_2CH_2Cl$ to a mixture of $CF_3CCl_2CClF_2$, $CF_3CCl_2CF_3$, $CF_3CClFCClF_2$, and $CF_3CClFCF_3$, the conversion of $CCl_3CH_2CHCl_2$ to a mixture of $CF_3CCl_2CClF_2$, $CF_3CCl_2CF_3$, $CF_3CClFCClF_2$, and $CF_3CClFCF_3$, the conversion of $CCl_3CHClCH_2Cl$ to a mixture of $CF_3CCl_2CClF_2$, $CF_3CCl_2CF_3$, $CF_3CClFCClF_2$, and $CF_3CClFCF_3$, the conversion of $CHCl_2CCl_2CH_2Cl$ to a mixture of $CF_3CCl_2CClF_2$, $CF_3CCl_2CF_3$, $CF_3CClFCClF_2$, and $CF_3CClFCF_3$, the conversion of $CCl_3CH_2CH_2Cl$ to a mixture of $CF_3CCl_2CHF_2$, $CF_3CClFCHF_2$, $CF_3CClFCClF_2$, and $CF_3CCl_2CF_3$, and the conversion of $CCl_3CH_2CHCl_2$ to a mixture of $CF_3CCl_2CHF_2$, $CF_3CClFCHF_2$, $CF_3CClFCClF_2$, and $CF_3CCl_2CF_3$.

Specific examples of vapor phase chlorofluorination reactions of unsaturated halogenated hydrocarbon compounds of the general formula $C_pH_eBr_fCl_gF_h$ and unsaturated hydrocarbon compounds of the general formula C_iH_j which may be carried out using the catalysts of this invention include the conversion of C_2H_4 to a mixture of CCl_3CClF_2, CCl_2FCCl_2F, $CClF_2CCl_2F$, CCl_3CF_3, CF_3CCl_2F, and $CClF_2CClF_2$, the conversion of C_2Cl_4 to a mixture of CCl_3CClF_2, CCl_2FCCl_2F, $CClF_2CCl_2F$, CCl_3CF_3, CF_3CCl_2F, and $CClF_2CClF_2$, and the conversion of C_3H_6 or $CF_3CCl{=}CCl_2$ to a mixture of $CF_3CCl_2CClF_2$, $CF_3CCl_2CF_3$, $CF_3CClFCClF_2$, and $CF_3CClFCF_3$.

Of note is a catalytic process for producing a mixture containing 2-chloro-1,1,1-trifluoroethane (i.e., CH_2ClCF_3 or HCFC-133a) by reaction of ethane with HF and Cl_2 in the vapor phase in the presence of the catalysts of this invention. The chlorofluorination of ethane is preferably conducted at about 150°C to about 450°C, preferably from about 300°C to about 400°C. The molar ratio of HF to ethane is preferably from about 3:1 to about 15:1 and the molar ratio of chlorine to ethane of from about 2:1 to 5:1. Preferred contacts times are from about 5 seconds to about 60 seconds. Oxygen in the form of air or co-fed with an inert diluent such

as nitrogen, helium, or argon may be added along with the reactants or as a separate catalyst treatment, if desired.

Also of note is a catalytic process for producing a mixture of 1,2,2-trichloro-1,1,3,3,3-pentafluoropropane (i.e., $CClF_2CCl_2CF_3$ or CFC-215aa), 2,2-dichloro-1,1,1,3,3,3-hexafluoropropane (i.e., $CF_3CCl_2CF_3$ or CFC-216aa), 1,2-dichloro-1,1,1,3,3,3-hexafluoropropane (i.e., $CClF_2CClFCF_3$ or CFC-216ba), and 2-chloro-1,1,1,2,3,3,3-heptafluoropropane (i.e., $CF_3CClFCF_3$ or CFC-217ba), by the chlorofluorination of a hexahalopropene of the formula $C_3Cl_{6-x}F_x$, wherein x equals 0 to 4. Preferred hexahalopropenes of the formula $C_3Cl_{6-x}F_x$ include 1,2,2-trichloro-3,3,3-trifluoro-1-propene (i.e., $CCl_2=CClCF_3$ or CFC-1213xa) and hexachloropropene (i.e., $CCl_2=CClCCl_3$). The mixture of CFC-215aa, -216aa, -216ba, and -217ba is produced by reacting the above unsaturated compounds with Cl_2 and HF in the vapor phase in the presence of the catalysts of this invention at temperatures from about 150°C to about 450°C, preferably about 250°C to 400°C.

The amount of HF fed to the reactor should be at least a stoichiometric amount based on the number of Cl substitutents in the $C_3Cl_{6-x}F_x$ starting material(s) and the desired composition of the final product. In the case of chlorofluorination of CFC-1213xa to a mixture of chlorofluoropropanes having an average number of fluorine substituents of six, the stoichiometric ratio of HF to CFC-1213xa is 3:1. Preferred ratios of HF to $C_3Cl_{6-x}F_x$ starting material(s) are typically in the range of about the stoichiometric ratio to about 30:1, more preferably from about 8:1 to 25:1.

The amount of chlorine fed to the reactor should be at least a stoichiometric amount. Preferred molar ratios of Cl_2 to CFC-1213xa are from about 1:1 to about 5:1.

Preferred contact times are from about 5 seconds to about 60 seconds.

Further information on the chlorofluorination of CFC-1213xa is provided in U.S. Patent Application _____[CL2108 US PRV] filed concurrently herewith, and hereby incorporated by reference herein in its entirety.

Mixtures of saturated hydrocarbon compounds and saturated halogenated hydrocarbon compounds and mixtures of unsaturated hydrocarbon compounds and unsaturated halogenated hydrocarbon compounds as well as mixtures comprising both saturated and

unsaturated compounds may be chlorofluorinated using the catalysts of the present invention. Specific examples of mixtures of saturated and unsaturated hydrocarbons and halogenated hydrocarbons that may be used include a mixture of $CCl_2=CCl_2$ and $CCl_2=CClCCl_3$, a mixture of $CHCl_2CCl_2CH_2Cl$ and $CCl_3CHClCH_2Cl$, a mixture of $CHCl_2CH_2CCl_3$ and $CCl_3CHClCH_2Cl$, a mixture of $CHCl_2CHClCCl_3$, $CCl_3CH_2CCl_3$, and $CCl_3CCl_2CH_2Cl$, a mixture of $CHF_2CH_2CF_3$ and $CHCl=CHCF_3$, and a mixture of $CH_2=CH_2$ and $CH_2=CHCH_3$.

Isomerization and Disproportionation

Included in this invention is a process for changing the fluorine distribution in a halogenated hydrocarbon compound by isomering said halogenated hydrocarbon compound in the presence of a catalyst composition comprising at least one chromium-containing component selected from the group consisting of the crystalline cobalt-substituted-chromium oxide described above and said cobalt-substituted alpha-chromium oxide which has been treated with a fluorinating agent.

Also included in this invention is a process for changing the fluorine distribution in a halogenated hydrocarbon compound by disproportionating said halogenated hydrocarbon compound in the vapor phase in the presence of a catalyst composition comprising at least one chromium-containing component selected from the group consisting of the crystalline cobalt-substituted alpha-chromium oxide described above and said cobalt-substituted alpha-chromium oxide which has been treated with a fluorinating agent.

Halogenated hydrocarbon compounds suitable as starting materials for the isomerization and disproportionation processes of this invention may be saturated or unsaturated. Saturated halogenated hydrocarbon compounds suitable for the isomerization and disproportionation processes of this invention include those of the general formula $C_nH_aBr_bCl_cF_d$, wherein n is an integer from 2 to 6, a is an integer from 0 to 12, b is an integer from 0 to 4, c is an integer from 0 to 13, d is an integer from 1 to 13, and the sum of a, b, c, and d is equal to 2n + 2, provided that a + b + c is at least 1. Unsaturated halogenated hydrocarbon compounds suitable for the isomerization and disproportionation processes of this invention include those of the general formula $C_pH_eBr_fCl_gF_h$, wherein p is an integer from 2 to 6, e is an integer from 0 to 10, f is an integer from 0 to 2, g is an integer from 0 to 12, h is an integer from 1 to 11, and the sum of e, f, g, and h is equal to 2p, provided that the sum of e + f + g is at least 1.

In one embodiment of the present invention, the fluorine distribution of a halogenated hydrocarbon compound is changed by rearranging the H, Br, Cl, and F substituents in the molecule (typically to a thermodynamically preferred arrangement) while maintaining the same number of the H, Br, Cl, and F substituents, respectively. This process is referred to herein as isomerization.

In another embodiment of the present invention, the fluorine distribution of a halogenated hydrocarbon compound is changed by exchanging at least one F substituent of one molecule of the halogenated hydrocarbon starting material with at least one H, Br and/or Cl substituent of another molecule of the halogenated hydrocarbon starting material so as to result in the formation of one or more halogenated hydrocarbon compounds having a decreased fluorine content compared to the halogenated hydrocarbon starting material and one or more halogenated hydrocarbon compounds having an increased fluorine content compared to the halogenated hydrocarbon starting material. This process is referred to herein as disproportionation.

In another embodiment of the present invention, both isomerization and disproportionation reactions may occur simultaneously.

Whether carrying out isomerization, disproportionation or both isomerization and disproportionation, the fluorine distribution of saturated compounds of the formula $C_nH_aBr_bCl_cF_d$ and/or unsaturated compounds of the formula $C_pH_eBr_fCl_gF_h$ may be changed in the presence of a catalyst composition comprising at least one chromium-containing component selected from the group consisting of the crystalline cobalt-substituted alpha-chromium oxide described above and said cobalt-substituted alpha-chromium oxide which has been treated with a fluorinating agent.

The isomerization and disproportionation reactions are typically conducted at temperatures of from about 150°C to 500°C, preferably from about 200°C to about 400°C. The contact time in the reactor is typically from about 1 to about 120 seconds and preferably from about 5 to about 60 seconds. The isomerization and disproportionation reactions may be carried out in the presence of an inert gas such as helium, argon, or nitrogen though this is not preferred. The isomerization and disproportionation reactions may be carried out in the presence of HF and HCl, but this is not preferred.

Specific examples of vapor phase isomerization reactions which may be carried out using the catalysts of this invention include the

conversion of $CClF_2CCl_2F$ to CCl_3CF_3, the conversion of $CClF_2CClF_2$ to CF_3CCl_2F, the conversion of CHF_2CClF_2 to CF_3CHClF, the conversion of CHF_2CHF_2 to CF_3CH_2F, the conversion of $CF_3CClFCClF_2$ to $CF_3CCl_2CF_3$, and the conversion of $CF_3CHFCHF_2$ to $CF_3CH_2CF_3$.

Specific examples of vapor phase disproportionation reactions which may be carried out using the catalysts of this invention include the conversion of $CClF_2CClF_2$ to a mixture of $CClF_2CCl_2F$, CCl_3CF_3, and CF_3CClF_2, and the conversion of $CHClFCF_3$ to a mixture of $CHCl_2CF_3$, and CHF_2CF_3.

Of note is a process for the conversion of a mixture of 2-chloro-1,1,2,2-tetrafluoroethane (i.e., CHF_2CClF_2 or HCFC-124a) and 2-chloro-1,1,1,2-tetrafluoroethane (i.e., CF_3CHClF or HCFC-124) to a mixture comprising 2,2-dichloro-1,1,1-trifluoroethane (i.e., $CHCl_2CF_3$ or HCFC-123) and 1,1,1,2,2-pentafluoroethane (i.e., CF_3CHF_2 or HFC-125) in addition to unconverted starting materials. The mixture comprising HFC-125 and HCFC-123 may be obtained in the vapor phase by contacting a mixture of HCFC-124a and -124 over the catalysts of this invention optionally in the presence of a diluent selected from the group consisting of HF, HCl, nitrogen, helium, argon, and carbon dioxide. The disproportionation is preferably conducted at about 150°C to about 400°C, more preferably about 250°C to about 350°C. If used, the diluent gas, may be present in a molar ratio of diluent to haloethane of from about 1:1 to about 5:1. Preferred contact times are from about 10 seconds to about 60 seconds.

Dehydrofluorination

Included in this invention is a process for decreasing the fluorine content of a halogenated hydrocarbon compound by dehydrofluorinating said halogenated hydrocarbon compound in the presence of a catalyst composition comprising at least one chromium-containing component selected from the group consisting of the crystalline cobalt-substituted alpha-chromium oxide described above and said cobalt-substituted alpha-chromium oxide which has been treated with a fluorinating agent.

Halogenated hydrocarbon compounds suitable as starting materials for the dehydrofluorination process of this invention are typically saturated. Saturated halogenated hydrocarbon compounds suitable for the dehydrofluorination processes of this invention include those of the general formula $C_nH_aF_d$, wherein n is an integer from 2 to 6, a is an integer from 1 to 12, d is an integer from 1 to 13, and the sum of a and d is

equal to 2n + 2. The fluorine content of saturated compounds of the formula $C_nH_aF_d$ may be decreased in the presence of a catalyst composition comprising at least one chromium-containing component selected from the group consisting of the crystalline cobalt-substituted alpha-chromium oxide described above and said cobalt-substituted alpha-chromium oxide which has been treated with a fluorinating agent. This decrease in fluorine content is typically associated with removal of hydrogen fluoride (HF) from the molecule and is referred to herein as dehydrofluorination.

The dehydrofluorination reactions are typically conducted at temperatures of from about 200°C to about 500°C, preferably from about 300°C to about 450°C. The contact time in the reactor is typically from about 1 to about 360 seconds and preferably from about 5 to about 120 seconds. Carrying out the dehydrofluorination reactions in the presence of an inert gas such as helium, argon, or nitrogen promotes the dissociation of the fluorinated carbon compound, but this practice can also lead to difficulties in separation and is not preferred.

The product of dehydrofluorination reaction consists of HF and the unsaturated fluorinated carbon compound resulting from loss of HF from the starting material. Specific examples of vapor phase dehydrofluorination reactions which may be carried out using the catalysts of this invention include the conversion of CH_3CHF_2 to CH_2=CHF, the conversion of CH_3CF_3 to CH_2=CF_2, the conversion of CF_3CH_2F to CF_2=CHF, the conversion of $CHF_2CH_2CF_3$ to CHF=$CHCF_3$, and the conversion of $CF_3CH_2CF_3$ to CF_3CH=CF_2.

Of note is a catalytic process for producing fluoroethene (i.e., CH_2=CHF or vinyl fluoride) by the dehydrofluorination of a 1,1-difluoroethane (i.e., CHF_2CH_3 or HFC-152a). A mixture comprising vinyl fluoride and unconverted HFC-152a may be obtained in the vapor phase by contacting HFC-152a over the catalysts of this invention optionally in the presence of a diluent selected from the group consisting of HF, nitrogen, helium, argon, and carbon dioxide. The dehydrofluorination is preferably conducted at about 150°C to about 400°C, more preferably about 250°C to about 350°C. If used, the diluent gas, may be present in a molar ratio of diluent to haloethane of from about 1:1 to about 5:1. Preferred contact times are from about 10 seconds to about 60 seconds.

Chlorodefluorination

Included in this invention is a process for decreasing the fluorine content of a halogenated hydrocarbon compound by reacting said halogenated hydrocarbon compound with hydrogen chloride (HCl) in the vapor phase in the presence of a catalyst composition comprising at least one chromium-containing component selected from the group consisting of the crystalline cobalt-substituted alpha-chromium oxide described above and said cobalt-substituted alpha-chromium oxide which has been treated with a fluorinating agent.

Halogenated hydrocarbon compounds suitable as starting materials for the chlorodefluorination processes of this invention may be saturated or unsaturated. Saturated halogenated hydrocarbon compounds suitable for the chlorodefluorination processes of this invention include those of the general formula $C_nH_aCl_cF_d$, wherein n is an integer from 1 to 6, a is an integer from 0 to 12, c is an integer from 0 to 13, d is an integer from 1 to 13, and the sum of a, c and d is equal to 2n + 2. Unsaturated halogenated hydrocarbon compounds suitable for the chlorodefluorination processes of this invention include those of the general formula $C_pH_eCl_gF_h$, wherein p is an integer from 2 to 6, e is an integer from 0 to 10, g is an integer from 0 to 12, h is an integer from 1 to 11, and the sum of e, g, and h is equal to 2p. The fluorine content of saturated compounds of the formula $C_nH_aCl_cF_d$ and/or unsaturated compounds of the formula $C_pH_eCl_gF_h$ may be decreased by reacting said compounds with HCl in the vapor phase in the presence of a catalyst composition comprising at least one chromium-containing component selected from the group consisting of the crystalline cobalt-substituted alpha-chromium oxide described above and said cobalt-substituted alpha-chromium oxide which has been treated with a fluorinating agent. Such a process is referred to herein as a vapor phase chlorodefluorination reaction. Chlorodefluorination is disclosed in U.S. Patent No. 5,345,017 and U.S. Patent No. 5,763,698 and the teachings of these two patents are hereby incorporated herein by reference.

The chlorodefluorination reactions are typically conducted at temperatures of from about 250°C to 450°C, preferably from about 300°C to about 400°C. The contact time in the reactor is typically from about 1 to about 120 seconds and preferably from about 5 to about 60 seconds. The reactions are most conveniently carried out at atmospheric or superatmospheric pressure.

Chlorodefluorinations involving saturated halogenated hydrocarbons are of particular note. The molar ratio of HCl to the saturated halogenated hydrocarbon compound is typically from about 1:1 to about 100:1, preferably from about 3:1 to about 50:1, and most preferably from about 4:1 to about 30:1. In general, with a given catalyst composition, the higher the temperature, the longer the contact time, and the greater the molar ratio of HCl to saturated halogenated hydrocarbon compound, the greater is the conversion to compounds having lower fluorine content. The above variables can be balanced, one against the other, so that the formation of chlorine- substituted products is maximized.

The product of chlorodefluorination reactions typically comprise unreacted HCl, HF, unconverted starting material, and saturated halogenated hydrocarbon compounds having a lower fluorine content than the starting material by virtue of the substitution of one or more fluorine substituents for chlorine. Specific examples of vapor phase chlorodefluorination reactions which may be carried out using the catalysts of this invention include the conversion of CHF_3 to a mixture of $CHCl_3$, $CHCl_2F$, and $CHClF_2$, the conversion of $CClF_2CClF_2$ to a mixture of CCl_3CCl_3, CCl_3CCl_2F, CCl_3CClF_2, CCl_2FCCl_2F, $CClF_2CCl_2F$, and CCl_3CF_3, the conversion of CF_3CClF_2 to a mixture of CCl_3CCl_3, CCl_3CCl_2F, CCl_3CClF_2, CCl_2FCCl_2F, $CClF_2CCl_2F$, CCl_3CF_3, $CClF_2CClF_2$, and CF_3CCl_2F, the conversion of $CF_3CCl_2CF_3$ to a mixture of $CF_3CCl_2CClF_2$, $CF_3CCl_2CCl_2F$, $CF_3CCl_2CCl_3$, and $CClF_2CCl_2CCl_3$, and the conversion of $CF_3CH_2CF_3$ to a mixture of $CCl_2{=}CHCF_3$, and $CCl_2{=}CClCF_3$.

Of note is a catalytic process for producing a mixture containing 1,1-dichloro-3,3,3-trifluoro-1-propene (i.e., $CCl_2{=}CHCF_3$ or HCFC-1223za) and 1,1,2-trichloro-3,3,3-trifluoro-1-propene (i.e., $CCl_2{=}CClCF_3$ or CFC-1213xa) by the chlorodefluorination of 1,1,1,3,3,3-hexafluoropropane (i.e., $CF_3CH_2CF_3$ or HFC-236fa) by reaction of HFC-236fa with HCl in the vapor phase in the presence of the catalysts of this invention. The reaction is preferably conducted from about 275°C to about 450°C, more preferably about 300°C to about 400°C with a molar ratio of HCl to HFC-236fa of preferably from about 3:1 to about 20:1. Preferred contacts times are from about 1 second to about 40 seconds. Oxygen in the form of air or co-fed with an inert diluent such as nitrogen, helium, or argon may be added along with the reactants or as a separate catalyst treatment, if desired.

The reaction products obtained by the processes of this invention can be separated by conventional techniques, such as with combinations including, but not limited to, scrubbing, decantation, or distillation. Some of the products of the various embodiments of this invention may form one or more azeotropes with each other or with HF.

The processes of this invention can be carried out readily using well known chemical engineering practices.

Utility

Several of the reaction products obtained through use of the catalysts disclosed herein will have desired properties for direct commercial use. For example, CH_2F_2 (HFC-32), CHF_2CF_3 (HFC-125), CHF_2CF_3 (HFC-125), CH_2FCHF_2 (HFC-134), $CF_3CH_2CF_3$ (HFC-236fa), and $CF_3CH_2CHF_2$ (HFC-245fa) find application as refrigerants, CH_2FCF_3 (HFC-134a) and CF_3CHFCF_3 (HFC-227ea) find application as propellants, CH_2FCHF_2 (HFC-134) and $CF_3CH_2CHF_2$ (HFC-245fa) find application as blowing agents, and CHF_2CF_3 (HFC-125), $CF_3CH_2CF_3$ (HFC-236fa), and CF_3CHFCF_3 (HFC-227ea) find application as fire extinguishants.

Other reaction products obtained through the use of this invention are used as chemical intermediates to make useful products. For example, CCl_3CF_3 (CFC-113a) can be used to prepare CFC-114a which can then be converted to CH_2FCF_3 (HFC-134a) by hydrodechlorination. Similarly, $CF_3CCl_2CF_3$ (CFC-216aa) can be used to prepare $CF_3CH_2CF_3$ (HFC-236fa) by hydrodechlorination and $CF_3CCl{=}CF_2$ (CFC-1215zc) can be used to prepare $CF_3CH_2CHF_2$ (HFC-245fa) by hydrogenation.

Without further elaboration, it is believed that one skilled in the art can, using the description herein, utilize the present invention to its fullest extent. The following specific embodiments are, therefore, to be construed as merely illustrative, and do not constrain the remainder of the disclosure in any way whatsoever.

EXAMPLES

Catalyst Characterization

Energy Dispersive Spectroscopy (EDS) and Transmission Electron Microscopy (TEM)

In these studies, the crystallites were analyzed using a Philips CM-20 high-resolution transmission electron microscope operated at an accelerating voltage of 200 kV and configured with an Oxford windowless EDS system with a Si(Li) elemental detector. In the EDS analyses, electron-transparent thin sections of samples were used to minimize

sample thickness effects such as fluorescence. Also, due to the similarity of their atomic masses, the X-ray absorption cross-sections for Cr, Co, and Ni were assumed to be the same (see the discussion by Zaluzec on pages 121 to 167 in *Introduction to Analytical Electron Microscopy* edited by J. J. Hren, J. I. Goldstein, and D. C. Joy (Plenum Press, New York,1979). The presence of copper in the EDS of Figures 1, 2, and 3 is due to the TEM grid and background in the microscope.

X-Ray Absorption Spectroscopy (XAS) and X-Ray Powder Diffraction (XRD)

XRD data were obtained and analyzed according to methods described by Warren in *X-Ray Diffraction* (Addison-Wesley, Reading, MA, 1969). XAS data were obtained at beamline 5BMD, DND-CAT, of the Advanced Photon Source, Argonne National Laboratory. XAS data were obtained and analyzed using the methods described in Koningsberger and Prins in *X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS and XANES* (John Wiley & Sons, New York, 1988). Spectra were obtained for the K edges of Cr, Co, and Ni. Cr edges were obtained in transmission geometry, while Co and Ni edges were obtained in fluorescence mode, due to their low concentrations.

The data in Table 2 represent bulk averages over all Co atoms. Coordination numbers are extracted from the radial distribution function obtained by Fourier transform of the extended x-ray absorption fine structure (EXAFS) region of the Co spectra. Oxidation states were obtained by fitting of sample near edge Co spectra to those of standards with known oxidation states.

Use of the Advanced Photon Source for acquiring XRD and XAS data was supported by the U. S. Department of Energy, Office of Basic Energy Sciences, under Contract No. W-31-109-Eng-38.

Catalyst Preparations

COMPARATIVE PREPARATION EXAMPLE 1

Preparation of 100% Chromium Catalyst (400°C)

A solution of 400 g $Cr(NO_3)_3[9(H_2O)]$ (1.0 mole) in 1000 mL of deionized water was treated dropwise with 477 mL of 7.4M aqueous ammonia raising the pH to about 8.5. The slurry was stirred at room temperature overnight. After re-adjusting the pH to 8.5 with ammonia, the mixture was poured into evaporating dishes and dried in air at 120°C. The resulting solid was then calcined in air at 400°C for 24 hours.

The 100% chromium oxide was studied by TEM and EDS. The product consisted of uniform crystallites of α-Cr_2O_3 with a narrow size range of about 20 nm. EDS indicated the presence of chromium and oxygen with no contaminants.

PREPARATION EXAMPLE 2

Preparation of 99%Chromium/1%Cobalt Catalyst (400°C)

A solution of 792.29 g $Cr(NO_3)_3[9(H_2O)]$ (1.98 moles) and 5.82 g $Co(NO_3)_2[6(H_2O)]$ (0.0200 mole) was prepared in 2000 mL of deionized water. The solution was treated dropwise with 955 mL of 7.4M aqueous ammonia which raised the pH to about 8.5. The slurry was stirred at room temperature overnight. The pH was adjusted to 8.5 the following day. The solid was then collected using two fritted funnels; the resulting solid in each funnel was washed with 15-20 liters of deionized water. The solids were dried in air at 120°C for 24 hours and then calcined in air at 400°C for 24 hours.

Analysis of the sample by TEM and EDS indicated the presence of α-Cr_2O_3 crystallites in the size range of 20-40 nm. Cobalt was present in the chromium oxide lattice.

PREPARATION EXAMPLE 3

Preparation of 98%Chromium/2%Cobalt Catalyst (400°C)

A solution of 784.30 g $Cr(NO_3)_3[9(H_2O)]$ (1.96 moles) and 11.64 g $Co(NO_3)_2[6(H_2O)]$ (0.040 mole) was prepared in 2000 mL of deionized water. The solution was treated dropwise with 950 mL of 7.4M aqueous ammonia which raised the pH from about 1.8 to about 8.5. The slurry was stirred at room temperature overnight and then evaporated to dryness in air at 110-120°C for 48 hours. The dried catalyst was divided in half. One half was calcined in air at 400°C for 24 hours.

The Cr/Co oxide was studied by TEM and EDS. The oxides consisted of crystallites in the range of 20-40 nm. The EDS spectra indicated a uniform distribution of cobalt throughout the α-Cr_2O_3 structure. Analysis of the sample by XRD and XAS confirmed that the crystallites had an α-Cr_2O_3 structure and that the average oxidation state of cobalt was 2.94. The amount of cobalt incorporation in the α-Cr_2O_3 lattice was in the range of 1.7 to 2.0 atom %.

PREPARATION EXAMPLE 4

Preparation of 98%Chromium/2%Cobalt Catalyst (900°C)

The other half of the dried catalyst prepared in Preparation Example 3 was calcined in air at 900°C for 24 hours.

PREPARATION EXAMPLE 5

Preparation of 98%Chromium/2%Cobalt Catalyst (400°C)

A solution of 784.29 g $Cr(NO_3)_3[9(H_2O)]$ (1.96 moles) and 11.64 g $Co(NO_3)_2[6(H_2O)]$ (0.040 mole) was prepared in 2000 mL of deionized water. The solution was treated dropwise with 950 mL of 7.4M aqueous ammonia until the pH reached about 8.5. The slurry was stirred at room temperature for 24 hours while maintaining the pH at 8.5. The slurry was then evaporated to dryness in air at 110-120°C with heating at 120°C continuing over the weekend. The dried catalyst was then calcined in air at 400°C for 24 hours.

PREPARATION EXAMPLE 6

Preparation of 98%Chromium/2%Cobalt Catalyst (550°C)

A solution of 1,010 g $Cr(NO_3)_3[9(H_2O)]$ (2.52 moles) and 14.6 g $Co(NO_3)_2[6(H_2O)]$ (0.050 mole) was prepared in 1000 mL of deionized water. The green solution was evaporated at a temperature of about 100°C until a thick, black precipitate formed. The solid was dried at 300-325°C on a hot plate. The solid was then transferred to a porcelain dish and calcined in a furnace at 550°C for 20 hours.

Analysis of the sample by TEM and EDS indicated the presence of crystals of the cobalt-substituted α-Cr_2O_3 with only minor increase in particle size due to the higher calcination temperature. The particle size of the spinel phase increased to about 20 to 50 nm compared with 10 to30 nm observed in the sample calcined at 400°C.

PREPARATION EXAMPLE 7

Preparation of 98%Chromium/2%Cobalt Catalyst (400°C)

$Cr(NO_3)_3[9(H_2O)]$ (50.5 g ,0.126 mole) and $Co(NO_3)_2[6(H_2O)]$ (0.73 g, 0.00251 mole) were weighed into a porcelain crucible and melted together with stirring in the open air. The mixture was heated to decomposition and then calcined in a furnace at 400°C for 24 hours.

Analysis of the sample by TEM and EDS indicated the presence of 100-150 nm crystals of cobalt-substituted α-Cr_2O_3 as well as a relatively large quantity of the spinel phase having a particle size of about 10 to 30 nm.

In a manner similar to that above, cobalt/chromium oxide compositions having the bulk composition 0.5 atom % cobalt/99.5 atom % chromium, 1.0 atom % cobalt/99 atom % chromium, 3 atom % cobalt/ 97 atom % chromium, and 4 atom % cobalt/96 atom % chromium were prepared and calcined at 400°C.

Thermogravimetric analysis of these five cobalt/chromium compositions indicated that calcination at 400°C resulted in incomplete decomposition of the nitrate precursors. The samples of the five compositions were re-calcined at 550°C for 12 hours. Analysis of these samples by XAS indicated the average oxidation state of cobalt was +3.0 to +3.2. The sample containing nominally 0.5 atom % cobalt was too dilute in cobalt for XAS work. The average oxidation state of chromium was +3.2; a phase containing a small amount of Cr^{+6} was also present. XRD and XAS data indicated the local structure around cobalt was consistent with its presence in an α-Cr_2O_3 lattice. A second phase is also present with very small particle size which is believed to be $CrCoO_3$.

PREPARATION EXAMPLE 8

Preparation of 97.8%Chromium/2.2%Cobalt Catalyst (550°C)

$Cr(NO_3)_3[9(H_2O)]$ (50.33 g ,0.126 mole) and $Co(NO_3)_2[6(H_2O)]$ (0.82 g, 0.00282 mole) were weighed into a porcelain crucible and melted together with stirring in the open air. The mixture was heated to decomposition and then calcined in a furnace at 550°C for 12 hours.

In a manner similar to that above, cobalt/chromium oxide compositions having the bulk composition 2.4 atom % cobalt/97.6 atom % chromium and 2.7 atom % cobalt/97.3 atom % chromium were prepared and calcined at 550°C.

Analysis of these three samples by XAS indicated the average oxidation state of cobalt was +3.1 to +3.2. The average oxidation state of chromium was +3.13 to +3.20 with a phase containing a small amount of Cr^{+6} also present. XRD and XAS data indicated the local structure around cobalt was consistent with its presence in an α-Cr_2O_3 lattice. A second phase is also present with very small particle size which is believed to be $CrCoO_3$.

PREPARATION EXAMPLE 9

Preparation of 98%Chromium/2%Cobalt Catalyst (550°C)

A solution of 1,010 g $Cr(NO_3)_3[9(H_2O)]$ (2.52 moles) and 14.6 g $Co(NO_3)_2[6(H_2O)]$ (0.0502 mole) was prepared in 1500 mL of deionized water. The solution was treated with 500 mL of 29 weight percent aqueous ammonia with mixing provided by a mechanical stirrer. The mixture was stirred for two hours and the pH stabilized at 6.0. The mixture was transferred to a large, ceramic dish. Water was driven off by heating. After most of the water had evaporated, the sample was heated to

250-300°C on a hot plate. The resulting solid was then transferred to a porcelain dish and calcined in a furnace at 550°C for 20 hours.

Analysis of the sample by TEM and EDS indicated that formation of the spinel phase was minimal by the precipitation technique. About 90% of the cobalt-substituted α-Cr_2O_3 phase consisted of crystallites in the size range of 20-40 nm with the remaining 10% being very large crystallites in the size range of 200-400 nm.

PREPARATION EXAMPLE 10

Preparation of 97%Chromium/3%Cobalt Catalyst (unwashed, 400°C)

A solution of 776.29 g $Cr(NO_3)_3[9(H_2O)]$ (1.94 moles) and 17.46 g $Co(NO_3)_2[6(H_2O)]$ (0.060 mole) was prepared in 2000 mL of deionized water. The solution was treated dropwise with 950 mL of 7.4M aqueous ammonia until the pH reached about 8.5. The slurry was stirred at room temperature for 24 hours and then evaporated to dryness in air at 110-120°C. The dried catalyst was ground to a powder and then calcined in air at 400°C for 24 hours. The surface area of the calcined product was 30.5 m^2/g.

PREPARATION EXAMPLE 11

Preparation of 97%Chromium/3%Cobalt Catalyst (washed; 400°C)

A solution of 776.29 g $Cr(NO_3)_3[9(H_2O)]$ (1.94 moles) and 17.46 g $Co(NO_3)_2[6(H_2O)]$ (0.060 mole) was prepared in 2000 mL of deionized water. The solution was treated dropwise with 955 mL of 7.4M aqueous ammonia which raised the pH to about 8.5. The slurry was stirred at room temperature overnight and the pH adjusted to 8.5 the following day. The solid was collected in two 3 L fritted funnels and each portion washed with 15-20 L of deionized water. The washed solid was then evaporated to dryness in air at 120°C for 24 hours and then calcined in air at 400°C for 24 hours. The surface area of the calcined product was 17.8 m^2/g.

The Cr/Co oxide was studied by TEM and EDS. The α-Cr_2O_3 phase consisted of crystallites in the range of 100 nm and the EDS spectrum indicated the presence of cobalt substituted into the lattice. This sample also contained a second phase consisting of crystallites in the size range of 10 nm. The EDS spectrum indicated that this phase contained comparable amounts of cobalt and chromium and was likely a spinel phase.

PREPARATION EXAMPLE 12

Preparation of 95%Chromium/5%Cobalt Catalyst (900°C)

A solution of 380.14 g $Cr(NO_3)_3[9(H_2O)]$ (0.95 moles) and 14.55 g $Co(NO_3)_2[6(H_2O)]$ (0.050 mole) was prepared in 1000 mL of deionized water. The solution was treated dropwise with 450 mL of 7.4M aqueous ammonia as the pH increased from about 1.7 to 8.4. The slurry was stirred at room temperature overnight and then evaporated to dryness in air at 120°C and held at that temperature overnight. The dried catalyst was ground to a powder and then calcined in air at 900°C for 20 hours.

PREPARATION EXAMPLE 13

Preparation of 95%Chromium/5%Cobalt Catalyst (400°C)

A solution of 760.28 g $Cr(NO_3)_3[9(H_2O)]$ (1.90 moles) and 29.10 g $Co(NO_3)_2[6(H_2O)]$ (0.10 mole) was prepared in 2000 mL of deionized water. The solution was treated dropwise with 950 mL of 7.4M aqueous ammonia which raised the pH to about 8.5. The slurry was stirred at room temperature overnight and then evaporated to dryness in air at 110-120°C for 48 hours. The dried catalyst was divided in half. One half was calcined in air at 400°C for 24 hours. The surface area of the calcined product was 33.6 m^2/g.

The Cr/Co 95/5 oxide was studied by TEM and EDS. The α-Cr_2O_3 phase consisted of crystallites in the range of 50 nm and the EDS spectrum indicated the presence of cobalt substituted into the lattice. This sample also contained small crystallites of a spinel phase. Analysis of the sample by XRD and XAS confirmed that the crystallites had an α-Cr_2O_3 structure and that the average oxidation state of cobalt was 2.84. The amount of cobalt incorporation in the α-Cr_2O_3 lattice was in the range of 3.8 to 4.4 atom %.

PREPARATION EXAMPLE 14

Preparation of 95%Chromium/5%Cobalt Catalyst (900°C)

The other half of the dried catalyst prepared in PREPARATION EXAMPLE 13 was calcined in air at 900°C for 24 hours.

PREPARATION EXAMPLE 15

Preparation of 95%Chromium/5%Cobalt Catalyst

(1.5 eq. excess NH_4NO_3, 400°C)

A solution of 760.28 g $Cr(NO_3)_3[9(H_2O)]$ (1.90 moles) and 29.10 g $Co(NO_3)_2[6(H_2O)]$ (0.10 mole) was prepared in 2000 mL of deionized water. The solution was treated dropwise with 950 mL of 7.4M aqueous ammonia; the pH reached 8.5. The slurry was stirred at room temperature

for 24 hours and then treated with a solution of 240.12 g NH_4NO_3 (3.0 moles). After stirring at room temperature for 2 hours, the mixture was evaporated to dryness in air at 120°C and held at that temperature over the weekend. The dried catalyst was ground to a powder with a mortar and pestle and then calcined in air at 400°C for 24 hours. The surface area of the calcined product was 36.5 m^2/g.

PREPARATION EXAMPLE 16

Preparation of 90%Chromium/10%Cobalt Catalyst (washed; 400°C)

A solution of 720.27 g $Cr(NO_3)_3[9(H_2O)]$ (1.80 moles) and 58.21 g $Co(NO_3)_2[6(H_2O)]$ (0.20 mole) was prepared in 2000 mL of deionized water. The solution was treated dropwise with 955 mL of 7.4M aqueous ammonia which raised the pH from about 2.1 to about 8.5. The slurry was stirred at room temperature overnight. The following day, the pH was the increased from 8.05 to 8.5 by addition of aqueous ammonia. The solid was collected in two 3 L fritted funnels and each portion washed with 15-20 L of deionized water. The washed solid was then evaporated to dryness in air at 120°C for 24 hours. The dried catalyst was then calcined in air at 400°C for 24 hours.

The Cr/Co 90/10 oxide was studied by TEM and EDS. The sample consisted of two phases. The α-Cr_2O_3 phase consisted of crystallites in the range of 100 nm and the EDS spectrum indicated the presence of cobalt in the lattice. This sample also contained a relatively large amount of a spinel-like phase in the form of 10 nm crystallites. Analysis of the sample by XRD and XAS indicated the sample was mostly an α-Cr_2O_3 structure and that the average oxidation state of cobalt was 2.63. The amount of cobalt incorporation in the α-Cr_2O_3 lattice was in the range of 4.5 to 5.9 atom %.

PREPARATION EXAMPLE 17

Preparation of 90%Chromium/10%Cobalt Catalyst
(3.3 eq. excess NH_4NO_3; 400°C)

A solution of 72.03 g $Cr(NO_3)_3[9(H_2O)]$ (0.18 mole) and 5.82 g $Co(NO_3)_2[6(H_2O)]$ (0.020 mole) was prepared in 200 mL of deionized water. The solution was brought to pH 8.5 treatment with 7.4M aqueous ammonia. The slurry was stirred at room temperature for 24 hours. The mixture was then treated with a solution of 48.02 g of NH_4NO_3 (0.60 mole) dissolved in 100 mL of water. The slurry was stirred for one hour and then dried at 120°C in air for about 90 hours. The dried solid was crushed to a

powder and then placed in covered dish and calcined at 400°C for 24 hours in air.

Analysis of the sample by XRD indicated the α-Cr_2O_3 structure of the primary crystalline phase had a lattice contraction consistent with the presence of Co^{+3} substitution for Cr^{+3}. The size range of the crystallites was about half of that observed in Preparation Example 16.

PREPARATION EXAMPLE 18

Preparation of 90%Chromium/10%Cobalt Catalyst

(6.7 eq. excess NH_4NO_3; 400°C)

The oxide preparation above was repeated except that the mixture of chromium/cobalt oxide/hydroxides was treated with a solution of 96.05 g of $NH_4(NO_3)$ (1.2 moles) dissolved in 200 mL of water.

Analysis of the sample by XRD indicated the α-Cr_2O_3 structure of the primary crystalline phase had a lattice contraction consistent with the presence of Co^{+3} substitution for Cr^{+3}. The size range of the crystallites was about half of that observed in Preparation Example 16.

General Procedure for Fluorocarbon Product Analysis

The following general procedure is illustrative of the method used for analyzing the products of fluorocarbon reactions. Part of the total reactor effluent was sampled on-line for organic product analysis using a gas chromatograph equipped a mass selective detector (GC-MS). The gas chromatography was accomplished with a 20 ft. (6.1 m) long x 1/8 in. (0.32 cm) diameter tubing containing Krytox® perfluorinated polyether on an inert carbon support. The helium flow was 30 mL/min. Gas chromatographic conditions were 60°C for an initial hold period of three minutes followed by temperature programming to 200°C at a rate of 6°C/minute.

The bulk of the reactor effluent containing organic products and also inorganic acids such as HCl and HF was treated with aqueous caustic prior to disposal.

All vapor reactions were conducted at a nominal pressure of one atmosphere.

Legend

12 is CCl_2F_2	13 is $CClF_3$
21 is $CHCl_2F$	22 is $CHClF_2$
23 is CHF_3	32 is CH_2F_2
112 is CCl_2FCCl_2F	112a is CCl_3CClF_2
113 is CCl_2FCClF_2	113a is CCl_3CF_3

114 is $CClF_2CClF_2$
115 is CF_3CClF_2
122 is $CHCl_2CClF_2$
123a is $CHClFCClF_2$
124 is $CHClFCF_3$
125 is CHF_2CF_3
133a is CH_2ClCF_3
134a is CH_2FCF_3
152a is CH_3CHF_2
1111 is $CClF=CCl_2$
1113 is $CF_2=CClF$
1122 is $CHCl=CF_2$
1140 is $CH_2=CHCl$
214 is $C_3Cl_4F_4$
215aa is $CF_3CCl_2CClF_2$
216aa is $CF_3CCl_2CF_3$
216ca is $CClF_2CF_2CClF_2$
217ba is $CF_3CClFCF_3$
218 is $CF_3CF_2CF_3$
224ba is $CF_3CClFCHCl_2$
225ba is $CHClFCClFCF_3$
225cb is $CClF_2CF_2CHClF$
226ca is CF_3CF_2CHClF
227ca is $CF_3CF_2CHF_2$
235bb is $CF_3CClFCH_2F$
235fa is $CF_3CH_2CClF_2$
244eb is CF_3CHFCH_2Cl
245fa is $CF_3CH_2CHF_2$
254fb is $CF_3CH_2CH_2F$
1213xa is $CF_3CCl=CCl_2$
1215 is C_3ClF_5
1222 is $C_3HCl_3F_2$
1223za is $CCl_2=CHCF_3$
1225zc is $CF_3CH=CF_2$
1234ze is E- and Z-$CHF=CHCF_3$
1326 is C_4HClF_6
TFE is $CF_2=CF_2$

114a is CF_3CCl_2F
116 is CF_3CF_3
123 is $CHCl_2CF_3$
123b is CHF_2CCl_2F
124a is CHF_2CClF_2
132a is CHF_2CHCl_2
134 is CHF_2CHF_2
143a is CH_3CF_3
1110 is $CCl_2=CCl_2$
1112a is $CF_2=CCl_2$
1120 is $CHCl=CCl_2$
1130 is $C_2H_2Cl_2$
1141 is $CHF=CH_2$
214ab is $CF_3CCl_2CCl_2F$
215bb is $CCl_2FCClFCF_3$
216ba is $CClF_2CClFCF_3$
216cb is $CCl_2FCF_2CF_3$
217ca is $CClF_2CF_2CF_3$
224aa is CF_3CCl_2CHClF
224ca $CClF_2CF_2CHCl_2$
225ca is $CF_3CF_2CHCl_2$
225da is $CF_3CHClCClF_2$
226da is $CF_3CHClCF_3$
227ea is CF_3CHFCF_3
235da is $CF_3CHClCHF_2$
236fa is $CF_3CH_2CF_3$
245eb is CF_3CHFCH_2F
253fb is $CF_3CH_2CH_2Cl$
263fb is $CF_3CH_2CH_3$
1214 is $C_3Cl_2F_4$
1215xc is $CF_3CCl=CF_2$
1223 is $C_3HCl_2F_3$
1224 is C_3HClF_4
1234yf is $CH_2=CFCF_3$
1316 is $C_4Cl_2F_6$
HFP is $CF_2=CFCF_3$

EXAMPLE 19

Fluorination of CF_3CHCl_2

Cobalt-substituted chromium oxide (Cr/Co 95/5, 29.04 g, 20 mL, -12 to +20 mesh (1.68 to 0.84 mm)), prepared as described in Preparation Example 15 was placed in a 5/8" (1.58 cm) diameter Inconel™ nickel alloy reactor tube heated in a fluidized sand bath. The catalyst was heated from 77°C to 175°C in a flow of nitrogen (25 cc/min, $4.2\times10^{-7}m^3/s$) over the course of about 1.2 hours. HF and nitrogen were then co-fed to the reactor at a flow rate of 50 cc/min ($8.3\times10^{-7}m^3/s$) each. After 1.5 hours, the nitrogen flow was decreased to 20 cc/min ($3.3\times10^{-7}m^3/s$) and the HF flow increased to 80 cc/min ($1.3\times10^{-6}m^3/s$). The reactor temperature was gradually increased to 413°C during a 5 hour period and maintained at 413°C for an additional 0.6 hour. At the end of this period, the HF flow was stopped and the reactor cooled to 300°C under 20 sccm ($3.3\times10^{-7}m^3/s$) nitrogen flow.

The catalyst prepared as above was placed in the reactor, purged with nitrogen and HF at 300°C. HF and HCFC-123 vapor were co-fed to the reactor in molar ratio of 6:1 at a contact time of 30 seconds. Analysis of the reactor effluent by GC-MS is given below.

Component	Mole %
HFC-125	26.7
HCFC-124	49.2
HCFC-124a	0.2
CFC-114a	1.4
HCFC-123	22.1

Other products included CFC-113a, CFC-113, CFC-115.

EXAMPLE 20

Fluorination of CF_3CHClF

Cobalt-substituted chromium oxide (Cr/Co 90/10, 6.75g, 4 mL, 12-20 mesh, (1.68 to 0.84 mm)), prepared as described in Preparation Example 16 was placed in a 1/2" (1.27 cm) diameter Inconel™ nickel alloy reactor tube heated in a furnace. The catalyst was heated from 200°C to 400°C in a flow of nitrogen (50 cc/min, $8.3\times10^{-7}m^3/s$) over the course of about 25 minutes, and then the temperature was lowered to 300°C while maintaining the nitrogen flow for an additional 80 minutes. The flow of nitrogen was reduced to 35 cc/min ($5.8\times10^{-7}m^3/s$) and HF was then admitted to the reactor at a flow rate of 12 cc/min ($2.0\times10^{-7}m^3/s$). After 35 minutes, the temperature was raised to 325°C. After 60 minutes it was

raised to 350°C. After 60 minutes it was raised to 375°C. After 90 minutes it was raised to 400°C. After 30 minutes it was raised to 425°C. After 20 minutes, the flow of nitrogen was reduced to 15 cc/min ($2.5\times10^{-7}m^3/s$) and the flow of HF was increased to 28 cc/min ($4.7\times10^{-7}m^3/s$). After 20 minutes, the flow of nitrogen was reduced to 5 cc/min ($8.3\times10^{-8}m^3/s$) and the flow of HF was increased to 36 cc/min ($6.0\times10^{-7}m^3/s$). After 20 minutes, the flow of nitrogen was shut off and the flow of HF was increased to 40 cc/min ($6.7\times10^{-7}m^3/s$), and this condition was maintained for 120 minutes. The reactor temperature was adjusted to 350°C and HF and HCFC-124 vapor were fed to the reactor in molar ratio of 2:1 at a contact time of 3.3 seconds. Analysis of the reactor effluent by GC-MS is given below.

Component	Mole %
HFC-125	19.1
CFC-115	48 ppm
HCFC-124	77.5
HCFC-124a	0.4
HCFC-123	3.0

EXAMPLE 21

Fluorination of CF_3CHClF

Cobalt-substituted chromium oxide which had been pre-treated with excess NH_4NO_3 (Cr/Co 90/10, 5.66g, 4 mL, 12-20 mesh, (1.68 to 0.84 mm)), prepared as described in PREPARATION EXAMPLE 18, was placed in a 1/2" (1.27 cm) diameter Inconel™ nickel alloy reactor tube heated in a furnace. The catalyst was heated from 200°C to 400°C in a flow of nitrogen (50 cc/min, $8.3\times10^{-7}m^3/s$) over the course of about 25 minutes, and then the temperature was lowered to 300°C while maintaining the nitrogen flow for an additional 80 minutes. The flow of nitrogen was reduced to 35 cc/min ($5.8\times10^{-7}m^3/s$) and HF was then admitted to the reactor at a flow rate of 12 cc/min ($2.0\times10^{-7}m^3/s$). After 35 minutes, the temperature was raised to 325°C. After 60 minutes it was raised to 350°C. After 60 minutes it was raised to 375°C. After 90 minutes it was raised to 400°C. After 30 minutes it was raised to 425°C. After 20 minutes, the flow of nitrogen was reduced to 15 cc/min ($2.5\times10^{-7}m^3/s$) and the flow of HF was increased to 28 cc/min ($4.7\times10^{-7}m^3/s$). After 20 minutes, the flow of nitrogen was reduced to 5 cc/min ($8.3\times10^{-8}m^3/s$) and the flow of HF was increased to 36 cc/min ($6.0\times10^{-7}m^3/$). After 20 minutes, the flow of nitrogen was shut off and the

flow of HF was increased to 40 cc/min ($6.7\times10^{-7}m^3/s$), and this condition was maintained for 120 minutes. The reactor temperature was adjusted to 350°C and HF and HCFC-124 vapor were fed to the reactor in molar ratio of 2:1 at a contact time of 3.3 seconds. Analysis of the reactor effluent by GC-MS is given below.

Component	Mole %
HFC-125	62.0
CFC-115	200 ppm
HCFC-124	23.3
HCFC-124a	0.2
HCFC-133a	0.3
FCFC-114a	0.1
HCFC-123	14.0
FCFC-113	0.1

EXAMPLE 22

Fluorination of $CCl_2=CCl_2$

Cobalt-substituted chromium oxide (Cr/Co 90/10, 32.26g, 20 mL, -12 to +20 mesh, (1.68 to 0.84 mm)), prepared as described in Preparation Example 16 was placed in a 5/8" (1.58 cm) diameter Inconel™ nickel alloy reactor tube heated in a fluidized sand bath. The catalyst was heated from 50°C to 246°C in a flow of nitrogen (50 cc/min, $8.3\times10^{-7}m^3/s$) over the course of about 1.6 hours. The catalyst was purged with 20 cc/min ($3.3\times10^{-7}m^3/s$) N_2 overnight at 175°C, then HF and N_2 were co-fed to the reactor at flow rates of 50 cc/min ($8.3\times10^{-7}m^3/s$) each at 175°C. After 1.3 h, the nitrogen flow was decreased to 20 cc/min ($3.3\times10^{-7}m^3/s$) and the HF flow increased to 80 cc/min ($6.3\times10^{-6}m^3/s$). The reactor temperature was gradually increased to 375°C over a 2 hour period, then treated with 10 cc/min N_2 ($1.7\times10^{-7}m^3/s$) and 90 cc/min ($1.5\times10^{-6}m^3/s$) HF at 409°C for an additional 2.3 hour. At the end of this period, the HF flow was stopped and the reactor cooled to 300°C under 20 sccm ($3.3\times10^{-7}m^3/s$) nitrogen flow.

The catalyst prepared as above was placed in the reactor, purged with nitrogen and HF at 325°C. The reactor temperature was adjusted to 375°C and HF and tetrachloroethylene vapor were fed to the reactor in molar ratio of 6:1 at a contact time of 15 seconds. Analysis of the reactor effluent by GC-MS is given below.

Component	Mole %
HFC-125	0.1

HCFC-124	1.9
HCFC-124a	0.3
CFC-114a	1.6
HCFC-123	8.6
HCFC-123a	1.4
HCFC-122	2.8
CFC-1112a	2.5
CFC-1111	9.8
HCC-1110	68.5

Other products included CFC-112, CFC-112a, CFC-113a, CFC-113, CFC-114a, HCFC-133a, HFC-23

EXAMPLE 23

Fluorination of a Mixture of $CF_3CF_2CHCl_2$ and $CClF_2CF_2CHClF$

Cobalt-substituted chromium oxide (Cr/Co 97/3, 28.57g, 20 mL, -12 to +20 mesh, (1.68 to 0.84 mm)), prepared as described in PREPARATION EXAMPLE 10, was placed in a 5/8" (1.58 cm) diameter Inconel™ nickel alloy reactor tube heated in a fluidized sand bath. The catalyst was purged with 25 cc/min ($4.2\times10^{-7}m^3/s$) nitrogen at 150C for 16 hours. The N_2 flow was increased to 50 cc/min ($8.3\times10^{-7}m^3/s$) at 175C for 0.5 hour. N_2 and HF were then co-fed to the reactor at flow rates of 50 cc/min ($8.3\times10^{-7}m^3/s$) each. After 1.2 hours, the nitrogen flow was decreased to 20 cc/min ($3.3\times10^{-7}m^3/s$) and the HF flow increased to 80 cc/min ($1.3\times10^{-6}m^3/s$). The reactor temperature was gradually increased to 300°C over a 5.7 hours period. The HF was turned off and the reactor purged with 20 cc/min ($3.3\times10^{-7}m^3/s$) nitrogen for about 16 hours. The flows of N_2 and HF were then established at 20 cc/min ($3.3\times10^{-7}m^3/s$) and 80 cc/min ($1.3\times10^{-6}m^3/s$), respectively, and the reactor temperature increased from 298°C to 410°C over 3.5 hours and then held at 410°C for 2.3 hours. At the end of this period, the HF flow was stopped and the reactor cooled to 300°C under 20 sccm ($3.3\times10^{-7}m^3/s$) nitrogen flow.

The reactor temperature was adjusted to 325°C and the vapor of HF and the HCFC-225cb/ca mixture (52.8 GC area % 225cb and 46.8 GC area % 225ca) were co-fed to the reactor in molar ratio of 4:1 at a contact time of 30 seconds. Analysis of the reactor effluent by GC-MS is given below.

Component	GC Area %
HCFC-225ca	7.5

HCFC-225cb	16.7
HCFC-224ca	4.0
HCFC-226ca	22.6
HCFC-226cb	30.2
HFC-227ca	14.8

Other products included CFC-217ca, HCFC-226ba, HCFC-226da, HCFC-1224, CFC-216, HCFC-225 isomers, CFC-215ca, HCFC-1223.

EXAMPLE 24

Fluorination of $CF_3CCl=CCl_2$

Cobalt-substituted chromium oxide (Cr/Co 98/2, 28.04g, 20 mL, -12 to +20 mesh, (1.68 to 0.84 mm)), prepared as described in Preparation Example 5, was placed in a 5/8" (1.58 cm) diameter Inconel™ nickel alloy reactor tube heated in a fluidized sand bath. The catalyst was heated from 90°C to 177°C in a flow of nitrogen (50 cc/min, $8.3\times10^{-7}m^3/s$) over the course of about 0.7 hour. HF and N_2 were then co-fed to the reactor at flow rates of 50 cc/min ($8.3\times10^{-7}m^3/s$) each. After 2 h, the nitrogen flow was decreased to 20 cc/min ($3.3\times10^{-7}m^3/s$) and the HF flow increased to 80 cc/min ($1.3\times10^{-6}m^3/s$). The reactor temperature was gradually increased to 298°C during a 3.5 hour period. The HF was turned off and the reactor purged with 20 cc/min ($3.3\times10^{-7}m^3/s$) N_2 overnight at 299°C. The following day, the N_2 and HF flows were established at 20 cc/min ($1.3\times10^{-7}m^3/s$) and 80 cc/min ($1.3\times10^{-6}m^3/s$), respectively, and the reactor temperature increased to 400°C over 1.7 hours. The reactor was held at 400-410°C for an additional 1.3 hours. At the end of this period, the HF flow was stopped and the reactor cooled to 300°C under 20 sccm ($3.3\times10^{-7}m^3/s$) nitrogen flow. HF and CFC-1213xa were then co-fed to the reactor as vapors in molar ratio of 20:1 at a contact time of 15 seconds. Analysis of the reactor effluent by GC-MS at a reactor temperature of 300°C is given below.

Component	GC Area %
HCFC-226da	90.0
CFC-216ba	0.2
CFC-216aa	4.3
CFC-217ba	1.0
CFC-1215	1.1

Other products included HFC-1225, CFC-217ca, CFC-114, CFC-114a, CFC-113, CFC-215, HCFC-225da.

EXAMPLE 25

Fluorination of $CF_3CCl=CCl_2$

Cobalt/chromium oxide (Cr/Co 98/2, calcined at 550°C, 32.0 g, 20 mL, -12 to +20 mesh, (1.68 to 0.84 mm)), prepared as described in PREPARATION EXAMPLE 6, was placed in a 5/8" (1.58 cm) diameter Inconel™ nickel alloy reactor tube heated in a fluidized sand bath. The catalyst was heated from 65°C to 176°C in a flow of nitrogen (50 cc/min, $8.3\times10^{-7}m^3/s$) over the course of about 0.8 hour. HF and N_2 were then co-fed to the reactor at flow rates of 50 cc/min ($8.3\times10^{-7}m^3/s$) each. After 0.6 hour the N_2 and HF flows were then adjusted to 20 cc/min ($3.3\times10^{-7}m^3/s$) and 80 cc/min ($1.3\times10^{-6}m^3/s$), respectively while the reactor temperature was increased to 411°C over 3 hours. The catalyst was held at 411°C for 0.75 hour. The N_2 and HF flows were then adjusted to 10 cc/min ($1.7\times10^{-7}m^3/s$) and 50 cc/min ($8.3\times10^{-7}m^3/s$), respectively, while the reactor temperature was maintained at 411°C for an additional 2 hours. At the end of this period, the HF flow was stopped and the reactor cooled to 295°C under 15 sccm ($2.5\times10^{-7}m^3/s$) nitrogen flow. Hydrogen fluoride and CFC-1213xa were co-fed to the reactor in a molar ratio of 20:1 at a contact time of 15 seconds. Analysis of the reactor effluent by GC-MS is given below.

	GC Area %
Component	300°C
HCFC-226da	25.4
CFC-216aa	20.8
CFC-1215	35.7
CFC-1214's	10.0
CFC-217ba	0.9
CFC-215aa	1.5
CFC-215bb	1.7
CFC-1213xa	2.4

Other products included HFP, CFC-216ba, CFC-216cb, CFC-114, CFC-114a, CFC-113, CFC-112.

COMPARATIVE EXAMPLE 26

Fluorination of $CF_3CCl=CCl_2$

A commercial sample of cobalt chromite ($CoCr_2O_4$, CAS Reg. No. [12016-69-2], 40.8 g, 20 mL, -12 to +20 mesh, (1.68 to 0.84 mm)),) was pelletized, sieved, and placed in a 5/8" (1.58 cm) diameter Inconel™ nickel alloy reactor tube heated in a fluidized sand bath. The catalyst was

heated from 80°C to 174°C in a flow of nitrogen (50 cc/min, $8.3\times10^{-7}m^3/s$) over the course of about 1.5 hours. HF and N_2 were then co-fed to the reactor at flow rates of 50 cc/min ($8.3\times10^{-7}m^3/s$) each. After 0.2 hour, the N_2 and HF flows were then adjusted to 20 cc/min ($3.3\times10^{-7}m^3/s$) and 80 cc/min ($1.3\times10^{-6}m^3/s$), respectively. The catalyst was then heated from 175°C to 401°C over the course of 3.2 hours. The HF flow was then ceased and the reactor cooled to 300°C under 20 sccm ($3.3\times10^{-7}m^3/s$) nitrogen flow. Hydrogen fluoride and CFC-1213xa were co-fed to the reactor in a molar ratio of 20:1 with a contact time of 15 seconds. Analysis of the reactor effluent by GC-MS is given below.

	GC Area %
Component	300°C
CFC-1213xa	97.9
CFC-112	0.5
CFC-215aa	0.2
CFC-1214's	0.5
CFC-1215	0.9

EXAMPLE 27

Chlorofluorination of Ethylene

The catalyst used in this experiment was that used in Example 24. The reactor temperature was adjusted to 250°C and the vapor of HF, ethylene, and chlorine were co-fed to the reactor in molar ratio of 12:1:1 at a contact time of 15 seconds. The GC-MS analysis of the reactor effluent at 250°C is shown below.

Component	GC Area %
Ethylene	6.1
HFC-1141	11.4
HFC-152a	47.3
HCC-1140	33.4

Other products included HFC-143a, COF_2, HCFC-142, HCC-1130, HCC-150.

EXAMPLE 28

Chlorofluorination of Ethane

The cobalt-substituted chromium oxide from Example 27 was used in this experiment. The reactor temperature was adjusted to 350°C and HF, CFC-1213xa, and chlorine were co-fed to the reactor in molar ratio of 10:1:4 at a contact time of 15 seconds. Analysis of the reactor effluent by GC-MS at a reactor temperature of 350°C is given below.

Component	GC Area %
HCFC-133a	37.0
HFC-143a	2.1
HFC-134	1.6
HCC-1120	22.9
HCC-1130 (two)	19.7
HCC-1140	1.3
HCC-1110	7.2
CFC-1111	1.2

Other products included HFC-1141, CFC-115, CFC-114a, HCFC-123a, HCFC-132a.

EXAMPLE 29

Chlorofluorination of $CF_3CCl=CCl_2$

Cobalt chromium oxide (Cr/Co 99/1, 29.0 g, 20 mL, -12 to +20 mesh, (1.68 to 0.84 mm)), prepared as described in Preparation Example 2, was placed in a 5/8" (1.58 cm) diameter Inconel™ nickel alloy reactor tube heated in a fluidized sand bath. The catalyst was heated from 52°C to 174°C in a flow of nitrogen (50 cc/min, $8.3\times10^{-7}m^3/s$) over the course of about one hour. HF and N_2 were then co-fed to the reactor at flow rates of 50 cc/min ($8.3\times10^{-7}m^3/s$) each for 2 hours; during this time there was a noticeable exotherm. The nitrogen flow was then decreased to 20 cc/min ($3.3\times10^{-7}m^3/s$) and the HF flow increased to 80 cc/min ($1.3\times10^{-6}m^3/s$). The reactor temperature was gradually increased to 407°C during a 3 hour period and held at 406°C for 1.3 hours. The HF flow was then stopped and the reactor cooled to 300°C under 20 sccm nitrogen flow. Chlorofluorination of CFC-1213xa began at 300°C with HF, CFC-1213xa, and chlorine co-fed to the reactor with a contact time of 15 seconds. GC-MS analysis of the reactor effluent at 320°C with a molar ratio of 20:1:4 (for HF, CFC-1213xa, and chlorine, respectively) and at 400°C with a molar ratio of 30:1:2 are given below.

	GC Area %	
Component	320°C	400°C
HCFC-226da	1.4	0.03
CFC-216ba	21.1	8.9
CFC-216aa	21.9	40.8
CFC-217ba	16.8	47.4
CFC-215aa	35.9	0.1
CFC-217ca	0.7	2.0

CFC-216cb	1.0	-

Other products included CFC-1215, CFC-114, CFC-114a, HCFC-225da, CFC-113.

EXAMPLE 30

Chlorofluorination of $CF_3CCl=CCl_2$

Cobalt/chromium oxide (Cr/Co 95/5, 21.8 g, 15 mL, -12 to +20 mesh, (1.68 to 0.84 mm)), prepared as described in Preparation Example 13 was placed in a 5/8" (1.58 cm) diameter Inconel™ nickel alloy reactor tube heated in a fluidized sand bath. The catalyst was heated from 52°C to 173°C in a flow of nitrogen (50 cc/min, $8.3\times10^{-7}m^3/s$) over the course of about 1 hour. HF and nitrogen were then co-fed to the reactor at flow rates of 2 cc/min ($4.2\times10^{-7}m^3/s$) and 75 cc/min ($1.25\times10^{-6}m^3/s$), respectively. After 2.2 hours, the nitrogen and HF flow rates were adjusted to 50 cc/min ($8.3\times10^{-7}m^3/s$) each and the reactor temperature was gradually increased to 299°C over 3 hours. The reactor was purged with 20 cc/min ($3.3\times10^{-7}m^3/s$) nitrogen overnight at 299°C. HF and nitrogen were then co-fed to the reactor at 80 cc/min ($1.3\times10^{-6}m^3/s$) and 20 cc/min ($3.3\times10^{-7}m^3/s$), respectively for 0.6 hour. The temperature of the reactor was then increased to 400°C over 2 hours. The nitrogen flow was reduced to 10 cc/min ($1.7\times10^{-7}m^3/s$) and the temperature increased to 410°C. After 1 hour, the temperature was adjusted to 280°C. Chlorofluorination of CFC-1213xa was begun at 280°C with HF, CFC-1213xa, and chlorine co-fed to the reactor in a molar ratio of 20:1:4 at a contact time of 15 seconds. GC-MS analyses of the reactor effluent at 320°C and 350°C are given below.

	GC Area Percent	
Component	320°C	350°C
HCFC-226da	1.2	0.4
CFC-216ba	23.2	26.6
CFC-216aa	19.5	35.3
CFC-217ba	8.7	9.8
CFC-215aa	44.5	25.8

Other products included CFC-217ca, CFC-1215, CFC-115, CFC-13, CFC-114, CFC-114a, CFC-216cb, CFC-113, CFC-214, CFC-215.

EXAMPLE 31

Chlorofluorination of $CF_3CCl=CCl_2$

Cobalt/chromium oxide pre-treated with excess ammonium nitrate (Cr/Co 95/5, 21.8 g, 15 mL, -12 to +20 mesh, (1.68 to 0.84 mm)), prepared

as described in Preparation Example 15 was placed in a 5/8" (1.58 cm) diameter Inconel™ nickel alloy reactor tube heated in a fluidized sand bath. The catalyst was heated from 77°C to 200°C in a flow of nitrogen (25 cc/min, $4.2\times10^{-7}m^3/s$) over the course of about 1.3 hours and held at this temperature for about 63 hours. HF and nitrogen were then co-fed to the reactor at flow rates of 50 cc/min ($8.3\times10^{-7}m^3/s$) each at 177°C. After 1.6 hours, the HF and nitrogen flow rates were adjusted to 80 cc/min ($1.3\times10^{-6}m^3/s$) and 20 cc/min ($3.3\times10^{-7}m^3/s$), respectively, and the temperature of the reactor increased to 413°C over 5 hours. After 0.7 hour at 413°C, the HF flow was stopped and the reactor purged with nitrogen overnight at 300°C. Chlorofluorination of CFC-1213xa was begun at 300°C with HF, CFC-1213xa, and chlorine co-fed to the reactor in a molar ratio of 20:1:4 at a contact time of 15 seconds. The GC-MS analyses of the reactor effluent at molar feed ratios of 20:1:4 at 320°C and 350°C and at 350°C with a molar feed ratio of 30:1:2 are given below.

	GC Area Percent		
	320°C	350°C	350°C
Component	20:1:4	20:1:4	30:1:2
HCFC-226da	1.8	0.9	3.0
CFC-216ba	17.6	18.6	12.2
CFC-216aa	22.5	34.1	42.9
CFC-217ba	18.1	20.4	27.6
CFC-215aa	36.7	23.8	12.0

Other products included CFC-217ca, CFC-1215, CFC-115, CFC-114, CFC-114a, CFC-216cb, CFC-113, CFC-214, CFC-215.

EXAMPLE 32

Chlorofluorination of $CF_3CCl=CCl_2$

Cobalt/chromium oxide (Cr/Co 97/3, 31.6 g, 20 mL, -12 to +20 mesh, (1.68 to 0.84 mm)), prepared as described in Preparation Example 11 was placed in a 5/8" (1.58 cm) diameter Inconel™ nickel alloy reactor tube heated in a fluidized sand bath. The catalyst was heated from 47°C to 174°C in a flow of nitrogen (50 cc/min, $8.3\times10^{-7}m^3/s$) over the course of about 0.8 hour. HF and nitrogen were then co-fed to the reactor at flow rates of 50 cc/min ($8.3\times10^{-7}m^3/s$) each. After 0.7 hours, the nitrogen and HF flow rates were adjusted to 20 cc/min ($3.3\times10^{-7}m^3/s$) and 80 cc/min ($1.3\times10^{-6}m^3/s$), respectively. After 1.7 hours at 175°C, the reactor temperature was gradually increased to 410°C over 3.4 hours. After 1 hour, the temperature was reduced from 410°C to 298°C, the HF flow

shut off, and the reactor purged with nitrogen over night. Chlorofluorination of CFC-1213xa was begun at 300°C with HF, CFC-1213xa, and chlorine vapor co-fed to the reactor in a molar ratio of 20:1:4 at a contact time of 15 seconds. The GC-MS analyses of the reactor effluent at 320°C and 350°C with molar feed ratios of 20:1:4 and at 400°C with molar feed ratios of 30:1:2 are given below.

	GC Area Percent		
Component	320°C	350°C	400°C
HCFC-226da	3.0	1.8	1.1
CFC-216ba	17.1	24.7	19.6
CFC-216aa	14.6	19.6	33.7
CFC-217ba	14.9	21.0	31.7
CFC-215aa	44.1	29.6	10.6
CFC-215bb	3.7	0.03	-

Other products included CFC-217ca, CFC-1215, CFC-115, CFC-13, CFC-114, CFC-114a, CFC-216cb, CFC-113, CFC-214, CFC-215.

EXAMPLE 33

Chlorofluorination of $CF_3CCl=CCl_2$

Cobalt/chromium oxide (Cr/Co 97/3, 28.2 g, 20 mL, -12 to +20 mesh, (1.68 to 0.84 mm)), prepared as described in Preparation Example 10 was placed in a 5/8" (1.58 cm) diameter Inconel™ nickel alloy reactor tube heated in a fluidized sand bath. The catalyst was purged with 25 cc/min ($8.3\times10^{-7}m^3/s$) nitrogen at 150C for 16 hours. The N_2 flow was increased to 50 cc/min ($8.3\times10^{-7}m^3/s$) at 175C for 0.5 hour. N_2 and HF were then co-fed to the reactor at flow rates of 50 cc/min ($8.3\times10^{-7}m^3/s$) each. After 1.2 hours, the nitrogen flow was decreased to 20 cc/min ($3.3\times10^{-7}m^3/s$) and the HF flow increased to 80 cc/min. The reactor temperature was gradually increased to 300°C over a 5.7 hours period. The HF was turned off and the reactor purged with 20 cc/min ($3.3\times10^{-7}m^3/s$) nitrogen for about 16 hours at 300°C. The flows of N_2 and HF were then established at 20 cc/min ($3.3\times10^{-7}m^3/s$) and 80 cc/min ($1.3\times10^{-6}m^3/s$), respectively, and the reactor temperature increased from 298°C to 410°C over 3.5 hours and then held at 410°C for 2.3 hours. At the end of this period, the HF flow was stopped and the reactor cooled to 300°C under 20 sccm nitrogen flow. Chlorofluorination of CFC-1213xa was begun at 300°C with HF, CFC-1213xa, and chlorine vapor co-fed to the reactor in a molar ratio of 20:1:4 at a contact time of 15 seconds. The

GC-MS analyses of the reactor effluent at 320°C and 350°C are given below.

	GC Area Percent	
Component	320°C	350°C
HCFC-226da	2.0	1.0
CFC-216ba	16.8	21.2
CFC-216aa	26.4	32.5
CFC-217ba	14.2	19.7
CFC-215aa	36.4	23.1

Other products included CFC-217ca, CFC-1215, HFC-1225, CFC-115, CFC-13, CFC-114, CFC-114a, CFC-216cb, CFC-113.

EXAMPLE 34

Chlorofluorination of $CF_3CCl=CCl_2$

Cobalt/chromium oxide (Cr/Co 98/2, calcined at 400°C, 21.06 g, 15 mL, -12 to +20 mesh, (1.68 to 0.84 mm)), prepared as described in PREPARATION EXAMPLE 3, was placed in a 5/8" (1.58 cm) diameter Inconel™ nickel alloy reactor tube heated in a fluidized sand bath. The catalyst was heated from 77°C to 176°C in a flow of nitrogen (50 cc/min, $8.3\times10^{-7}m^3/s$) over the course of about 1.7 hours. HF and N_2 were then co-fed to the reactor at flow rates of 50 cc/min ($8.3\times10^{-7}m^3/s$) each. After 1 hour the temperature was increased to 326°C over 3 hour while maintaining the HF and N_2 flows at 50 cc/min ($8.3\times10^{-7}m^3/s$). The N_2 and HF flows were then adjusted to 25 cc/min ($4.2\times10^{-7}m^3/s$) and 50 cc/min ($8.3\times10^{-7}m^3/s$), respectively, while the reactor temperature was increased to 401°C over 1 hour. The N_2 and HF flows were then adjusted to 10 cc/min and 50 cc/min ($8.3\times10^{-7}m^3/s$), respectively, while the reactor temperature was maintained at 401°C for 1 hour. At the end of this period, the HF flow was stopped and the reactor cooled to 280°C under 20 sccm nitrogen flow. Chlorofluorination of CFC-1213xa was begun at 280°C with HF, CFC-1213xa, and chlorine vapor co-fed to the reactor in a molar ratio of 20:1:4 at a contact time of 15 seconds. The GC-MS data for the reactor effluent at 320°C (20:1:4) and at 400°C (molar feed ratio 30:1:2; contact time =15 second) are given below.

	GC Area Percent	
Component	320°C	400°C
HCFC-226da	1.7	0.02
CFC-216ba	23.1	4.9
CFC-216aa	19.0	46.4

CFC-216cb	0.4	-
CFC-217ba	15.3	46.6
CFC-215aa	38.3	0.03
CFC-215bb	0.1	-
CFC-214ab	-	-

Other products included CFC-217ca, CFC-1215, CFC-115, CFC-114, CFC-114a, CFC-113, CFC-1213xa, CFC-112

EXAMPLE 35

Chlorofluorination of $CF_3CCl=CCl_2$

Cobalt/chromium oxide (Cr/Co 98/2, calcined at 900°C, 27.52 g, 15 mL, -12 to +20 mesh, (1.68 to 0.84 mm)), prepared as described in Preparation Example 4, was placed in a 5/8" (1.58 cm) diameter Inconel™ nickel alloy reactor tube heated in a fluidized sand bath. The catalyst was heated from 96°C to 174°C in a flow of nitrogen (50 cc/min, $8.3\times10^{-7}m^3/s$) over the course of about 0.5 hour. HF and N_2 were then co-fed to the reactor at flow rates of 50 cc/min ($8.3\times10^{-7}m^3/s$) each. After 0.3 hour at 175°C, the flows of HF and N_2 were adjusted to 80 cc/min ($1.3\times10^{-6}m^3/s$) and 20 cc/min ($3.3\times10^{-7}m^3/s$), respectively, and the temperature was then increased to 400°C over 5 hours. At the end of this period, the HF flow was stopped and the reactor cooled to 300°C under 20 sccm ($3.3\times10^{-7}m^3/s$) nitrogen flow. Chlorofluorination of CFC-1213xa was begun at 300°C with HF, CFC-1213xa, and chlorine vapor co-fed to the reactor in a molar ratio of 20:1:4 at a contact time of 15 seconds. The GC-MS analyses of the reactor effluent at 320°C and 400°C are given below.

	GC Area Percent	
Component	320°C	400°C
HCFC-226da	0.4	0.1
CFC-216ba	9.2	34.9
CFC-216aa	19.6	26.6
CFC-216cb	2.0	2.4
CFC-217ba	10.4	14.8
CFC-215aa	23.9	17.5
CFC-215bb	28.6	1.6
CFC-214ab	3.4	0.04

Other products included CFC-217ca, CFC-1215, CFC-115, CFC-114, CFC-114a, CFC-113, CFC-1213xa, CFC-112

EXAMPLE 36

Chlorofluorination of $CF_3CCl=CCl_2$

Hydrogen fluoride, CFC-1213xa, and chlorine were co-fed to the reactor containing the catalyst in Example 25 with a contact time of 15 seconds. The GC-MS analyses of the reactor effluent at 320°C (molar ratio of feed gases HF:1213xa:Cl_2 = 20:1:4) and 375°C (molar ratio of feed gases HF:1213xa:Cl_2 = 30:1:2) are given below.

	GC Area Percent	
Component	320°C	375°C
CFC-217ba	11.0	22.1
CFC-216aa	22.4	27.5
CFC-216ba	15.5	33.8
CFC-216cb	2.3	3.1
HCFC-226da	0.7	0.5
CFC-215aa	27.6	9.6
CFC-215bb	18.9	1.5
CFC-1213xa	-	-

Other products included CFC-115,CFC-217ca, CFC-1215, CFC-114, CFC-114a, CFC-1214's, CFC-113, CFC-112, CFC-214ab.

EXAMPLE 37

Chlorofluorination of $CF_3CCl=CCl_2$

Cobalt/chromium oxide (Cr/Co 98/2, calcined at 550°C, 29.4 g, 20 mL, -12 to +20 mesh, (1.68 to 0.84 mm)), prepared as described in Preparation Example 9, was placed in a 5/8" (1.58 cm) diameter Inconel™ nickel alloy reactor tube heated in a fluidized sand bath. The catalyst was purged with nitrogen (50 cc/min, $8.3\times10^{-7}m^3/s$) at 174°C for about 72 hours. HF and N_2 were then co-fed to the reactor at flow rates of 50 cc/min ($8.3\times10^{-7}m^3/s$) each. After 0.8 hour at 175°C, the flows of HF and N_2 were adjusted to 80 cc/min ($1.3\times10^{-6}m^3/s$) and 20 cc/min ($3.3\times10^{-7}m^3/s$), respectively, and the temperature was then increased to 400°C over 4.3 hours. The flows of HF and N_2 were adjusted to 50 cc/min ($8.3\times10^{-7}m^3/s$) and 10 cc/min ($1.7\times10^{-7}m^3/s$), respectively, and the reactor held at 406°C for an additional 1.7 hours. At the end of this period, the HF flow was stopped and the reactor cooled to 300°C under 20 sccm ($3.3\times10^{-7}m^3/s$) nitrogen flow. Chlorofluorination of CFC-1213xa was begun at 300°C with HF, CFC-1213xa, and chlorine vapor co-fed to the reactor in a molar ratio of 20:1:4 at a contact time of 15 seconds. The GC-MS analyses of the reactor effluent at 300°C (molar ratio of feed gases

HF:1213xa:Cl_2 = 20:1:4) and 400°C (molar ratio of feed gases HF:1213xa:Cl_2 = 30:1:2) are given below.

	GC Area Percent	
Component	300°C	400°C
CFC-217ba	11.1	36.7
CFC-216aa	18.7	36.6
CFC-216ba	18.4	21.7
CFC-216cb	1.6	-
HCFC-226da	1.3	0.2
CFC-215aa	44.8	2.6
CFC-215bb	2.6	-
CFC-1213xa	-	-

Other products included FC-218, CFC-13, CFC-115,CFC-217ca, CFC-1215, CFC-114, CFC-114a, CFC-1214's, CFC-113, CFC-214ab.

COMPARATIVE EXAMPLE 38

Chlorofluorination of $CF_3CCl=CCl_2$

Hydrogen fluoride, CFC-1213xa, and chlorine were co-fed to the reactor containing the HF-treated cobalt chromite catalyst from Comparative Example 26; the contact time of 15 seconds. The GC-MS analysis of the reactor effluent at 375°C (molar ratio of feed gases HF:1213xa:Cl_2 = 20:1:4) is given below.

	GC Area Percent
Component	375°C
CFC-217ba	0.2
CFC-216aa	0.6
CFC-216ba	0.4
CFC-216cb	3.1
CFC-215aa	10.5
CFC-215bb	24.9
CFC-214ab	27.4
CFC-1215	1.0
CFC-1214's	12.5
CFC-1213xa	21.6

Other products included CFC-115,CFC-216cb, CFC-114, CFC-114a, CFC-1214's, CFC-112, CFC-214ab.

COMPARATIVE EXAMPLE 39

Chlorofluorination of $CF_3CCl=CCl_2$

100% Chromium(III) oxide (calcined at 400°C, 27.8 g, 20 mL, -12 to +20 mesh, (1.68 to 0.84 mm)), prepared as described in Comparative Preparation Example 1 was placed in a 5/8" (1.58 cm) diameter Inconel™ nickel alloy reactor tube heated in a fluidized sand bath. The catalyst was heated from 77°C to 200°C in a flow of nitrogen (50 cc/min, $8.3\times10^{-7}m^3/s$) over the course of about an hour. The catalyst was then purged overnight with nitrogen (20 cc/min, $3.3\times10^{-7}m^3/s$) at 174°C. HF and nitrogen were then co-fed to the reactor at flow rates of 50 cc/min ($8.3\times10^{-7}m^3/s$) each at 175°C. After an hour, the HF and nitrogen flow rates were adjusted to 80 cc/min ($1.3\times10^{-6}m^3/s$) and 20 cc/min ($3.3\times10^{-7}m^3/s$), respectively, and the temperature of the reactor increased to 410°C over 3.6 hours. The HF flow was stopped and the reactor purged with nitrogen overnight at 300°C. Chlorofluorination of CFC-1213xa was begun at 300°C with HF, CFC-1213xa, and chlorine vapor co-fed to the reactor in a molar ratio of 20:1:4 at a contact time of 15 seconds. The GC-MS analyses of the reactor effluent at 300°C and at 400°C (molar feed ratio = 30:1:2) are given below.

	GC Area Percent	
Component	300°C	400°C
HCFC-226da	2.4	0.03
CFC-216ba	21.6	6.4
CFC-216aa	19.8	67.4
CFC-217ba	11.1	24.1
CFC-217ca	0.4	1.2
CFC-215aa	42.9	0.2

Other products included FC-218, CFC-1215, CFC-115, CFC-114, CFC-114a, CFC-216cb, CFC-113, CFC-112.

EXAMPLE 40

Isomerization of a 1:1 $CF_3CClFCClF_2$ /$CF_3CCl_2CF_3$ Mixture

The catalyst used in Example 34 was returned to the reactor and purged with nitrogen up to 350°C. A mixture of CFC-216ba/216aa (50.2 GC area % 216ba and 49.8 GC area % 216aa) and nitrogen were then co-fed to the reactor in molar ratio of 1:4 with a contact time of 30 seconds. The GC-MS analyses of the reactor effluent are given below.

Component	GC Area %
CFC-216ba	0.75
CFC-216aa	84.0

CFC-217ba	7.6
CFC-215aa	1.0
CFC-1213xa	3.9
CFC-1215	0.60

Other products included CFC-115, FC-218, CFC-217ca, CFC-114, CFC-114a, CFC-216cb, HCFC-226da, HCFC-225da, CFC-1214, CFC-215bb.

EXAMPLE 41

Fluorination of a $CF_3CHClF/CClF_2CHF_2$ Mixture

Cobalt-substituted chromium oxide (Cr/Co 95/5, 29.04g, 20 mL, -12 to +20 mesh, (1.68 to 0.84 mm)), prepared as described in PREPARATION EXAMPLE 15 was placed in a 5/8" (1.58 cm) diameter Inconel™ nickel alloy reactor tube heated in a fluidized sand bath. The catalyst was heated from 77°C to 175°C in a flow of nitrogen (25 cc/min, $3.3\times10^{-7}m^3/s$) over the course of about 1.2 hours. HF and nitrogen were then co-fed to the reactor at a flow rate of 50 cc/min ($8.3\times10^{-7}m^3/s$) each. After 1.5 hours, the nitrogen flow was decreased to 20 cc/min ($3.3\times10^{-7}m^3/s$) and the HF flow increased to 80 cc/min ($1.3\times10^{-6}m^3/s$). The reactor temperature was gradually increased to 413°C during a 5 hour period and maintained at 413°C for an additional 0.6 hour. At the end of this period, the HF flow was stopped and the reactor cooled to 300°C under 20 sccm nitrogen flow. HF and a mixture of HCFC-124 and HCFC-124a (52.1 GC area % 124a and 44.2 GC area % 124) vapor were co-fed to the reactor in molar ratio of 4:1 at a contact time of 10 seconds. The GC-MS analysis of the reactor effluent at 300°C is given below.

Component	Mole %
HFC-125	44.1
HCFC-124	24.7
HCFC-124a	25.0
CFC-133a	0.9
HCFC-123	2.7

Other products included impurities in starting material: HFC-32, HFC-143a, HFC-134a, HFC-134 and by-products: HFC-23, CFC-115, CFC-114a, HCFC-123a, HCFC-123b, CFC-113.

EXAMPLE 42

Disproportionation of a $CF_3CHClF/CClF_2CHF_2$ Mixture

Nitrogen and a mixture of HCFC-124 and HCFC-124a (52.1 GC area % 124a and 44.2 GC area % 124) were co-fed to the reactor containing the catalyst used in Example 41. The molar ratio of nitrogen to

124/124a mixture was 4:1 and the contact time was 10 seconds. The GC-MS analyses of the reactor effluent at 250°C and 300°C are given below.

	GC Mole %	
Component	250°C	300°C
HFC-125	24.6	55.2
HCFC-124	19.9	12.1
HCFC-124a	37.7	1.7
CFC-133a	1.6	2.1
HCFC-123	13.9	18.1
HCFC-123a	0.3	0
HCC-1110	-	4.7
HCC-1120	0.8	1.7
CFC-1111	0.2	2.5

Other products included HFC-23, HFC-32 HFC-143a, CFC-115, CFC-114a, HCFC-123b, CFC-113, HCFC-122.

EXAMPLE 43

Isomerization and Disproportionation of a $CClF_2CCl_2F/CF_3CCl_3$ Mixture

Nitrogen and a mixture of CFC-113 and CFC-113a (52.9 GC mole % 113a and 47.1 GC mole % 113) were co-fed to the reactor containing the catalyst used in Example 42. The molar ratio of nitrogen to 113/113a mixture was 4:1 and the contact time was 15 seconds. The GC-MS analyses of the reactor effluent at 150°C and 300°C are given below.

	Mole %	
Component	150°C	300°C
CFC-115	-	1.7
CFC-114	-	6.2
CFC-114a	21.2	24.5
CFC-1112a	10.4	8.5
CFC-113	27.2	10.4
CFC-113a	30.0	33.3
CFC-112/112a	10.7	9.8
HCC-1110	0.03	4.7

Other products included CFC-13, HCFC-1122, CFC-1113, CFC-1111, CFC-1316.

EXAMPLE 44

Disproportionation of CF_3CCl_2F

Nitrogen and CFC-114a (99.95 GC mole % 114a) were co-fed to the reactor containing the catalyst used in EXAMPLE 43 in a molar ratio of

4:1 with a contact time of 15 seconds. The GC-MS analyses of the reactor effluent at 250°C and 350°C are given below.

	Mole %	
Component	250°C	350°C
CFC-115	18.5	38.1
CFC-114	-	2.3
CFC-114a	64.6	30.6
CFC-1112a	0.2	0.7
CFC-113	0.03	0.7
CFC-113a	15.8	24.6
CFC-112/112a	-	0.2
HCC-1110	0.04	1.8

Other products included CFC-13, FC-116, HCFC-1122, CFC-1113, HCFC-123, CFC-1111, CFC-1316.

EXAMPLE 45

Disproportionation and Isomerization of a $CClF_2CClF_2/CF_3CClF_2$ Mixture

Nitrogen and a mixture of CFC-114 and CFC-114a (87.3 GC mole % 114 and 12.6 GC mole % 114a) were co-fed to the reactor containing the catalyst used in EXAMPLE 44. The molar ratio of nitrogen to 114/114a mixture was 4:1 and the contact time was 15 seconds. The GC-MS analyses of the reactor effluent at 300°C and 350°C are given below.

	Mole %	
Component	300°C	350°C
CFC-115	13.6	30.5
CFC-114	65.9	34.0
CFC-114a	11.0	18.1
CFC-1112a	1.4	1.9
CFC-113	4.8	4.4
CFC-113a	2.0	6.6
CFC-112/112a	0.2	0.4
HCC-1110	0.4	3.0

Other products included HFC-23, CFC-13, FC-116, HCFC-1122, CFC-1113, CFC-1111.

EXAMPLE 46

$CF_3CH_2CF_3$ Dehydrofluorination

Nitrogen and HFC-236fa were co-fed to the reactor containing the catalyst used in EXAMPLE 45. The molar ratio of nitrogen to 236fa was

4:1 and the contact time was 15 seconds. The GC-MS analyses of the reactor effluent at 300°C and 350°C are given below.

	Mole %	
Component	300°C	350°C
HFC-236fa	91.0	81.5
HFC-1225zc	7.2	17.1

Other products included HFC-143a, CFC-1215, HCFC-226da, HCFC-1224, HCFC-1326, HCFC-1223, CFC-216aa, CFC-217ba.

EXAMPLE 47

CH_3CHF_2 Dehydrofluorination

Nitrogen and HFC-152a were co-fed to the reactor containing the catalyst used in Example 45. The molar ratio of nitrogen to 152a was 4:1 and the contact time was 15 seconds. The GC-MS analyses of the reactor effluent at 250°C and 350°C are given below.

	Mole %	
Component	250°C	350°C
HFC-152a	63.1	16.7
HFC-1141	36.4	82.0

Other products included HCFC-151a, HCC-1140, ethylene, methane.

EXAMPLE 48

Isomerization of Hexafluorocyclopropane

The catalyst used in Example 34 (15 mL, 21.35 g) was returned to the reactor and purged with nitrogen at 350°C followed by HCl. Nitrogen and hexafluorocyclopropane were then co-fed to the reactor in a 2:1 molar ratio; the contact time was 30 seconds. The GC-MS analysis of the reactor effluent at 150°C is given below.

	GC Area %
Component	150°C
HFP	98.0
TFE	1.1
HFC-23	0.4
HFC-227ea	0.2

Other products included HFC-125, CFC-217ba, FC-1318my, PFIB, CFC-1215's.

EXAMPLE 49

Chlorodefluorination of Trifluoromethane

The catalyst used in Example 33 (5 mL, 7.1 g) was returned to the reactor and purged with nitrogen at 300°C. Anhydrous hydrogen chloride

and trifluoromethane (HFC-23) were then co-fed to the reactor in a 20:1 molar ratio; the contact time was 5 seconds. The GC-MS analysis of the reactor effluent at 325°C is given below.

Component	GC Area %
HFC-23	71.9
HCFC-22	6.3
HCFC-21	2.6
HCC-20	18.2
CFC-13	0.7
CFC-12	0.2

EXAMPLE 50

Chlorodefluorination of 1,1,1,3,3,3-Hexafluoropropane

Anhydrous hydrogen chloride and 1,1,1,3,3,3-hexafluoropropane (HFC-236fa) were co-fed in a 10:1 molar ratio to the reactor containing the catalyst used in EXAMPLE 49; the contact time was 10 seconds. The GC-MS analysis of the reactor effluent at 325°C is given below.

Component	GC Area %
HFC-236fa	49.8
HFC-1225zc	0.9
HCFC-1224 (two)	4.0
HCFC-235fa	0.7
HCFC-1223za	40.0
CFC-1213xa	3.7

Other products included HFC-143a, CFC-114/114a, CFC-1214, HCC-1120, HCFC-1222, HCC-1110.

Additional Catalyst Preparation - PREPARATION EXAMPLE 51

Preparation of 98%Chromium/2%Cobalt (550°C)

$[Cr(NH_3)_6]Cl_3$ (16.7684 g, 64.4 mmoles) and $[Co(NH_3)_6]Cl_3$ (0.3513g, 1.31 mmole) were dissolved in deionized water. Aqueous ammonium hydroxide was then added to the solution until precipitation was complete. The resulting precipitate was filtered and dried in air at 110°C for 12 hours. The resulting product was ground thoroughly in an agate mortar and then heated at 550°C in air for 12 hours.

Analysis of the sample by XRD indicated a predominant phase having α-Cr_2O_3 structure; and TEM and EDS indicated a small amount of a spinel phase containing cobalt and chromium. The cobalt-containing α-Cr_2O_3 phase was present in the form of 200-400 nm crystals. XAS indicated that cobalt was completely incorporated into the α-Cr_2O_3 lattice.

CLAIMS

What is claimed is:

1. A crystalline alpha-chromium oxide where from about 0.05 atom % to about 6 atom % of the chromium atoms in the alpha-chromium oxide lattice are replaced by trivalent cobalt atoms.

2. . A chromium-containing catalyst composition comprising as a chromium-containing component the crystalline cobalt-substituted alpha-chromium oxide of Claim 1.

3. A chromium-containing catalyst composition comprising a chromium-containing component prepared by treating the crystalline cobalt-substituted alpha-chromium oxide of Claim 1 with a fluorinating agent.

4. A process for changing the fluorine distribution in a hydrocarbon or a halogenated hydrocarbon in the presence of a catalyst, characterized by:

using as the catalyst a composition comprising at least one chromium-containing component selected from the group consisting of the crystalline cobalt-substituted alpha-chromium oxide of Claim 1 and a crystalline cobalt-substituted alpha-chromium oxide of Claim 1 which has been treated with a fluorinating agent.

5. The process of Claim 4 wherein the fluorine content of a halogenated hydrocarbon compound or an unsaturated hydrocarbon compound is increased by reacting said compound with hydrogen fluoride in the vapor phase in the presence of said catalyst composition.

6. The process of Claim 4 wherein the fluorine content of a halogenated hydrocarbon compound or a hydrocarbon compound is increased by reacting said compound with HF and Cl_2 in the vapor phase in the presence of said catalyst composition.

7. The process of Claim 4 wherein the fluorine distribution in a halogenated hydrocarbon compound is changed by isomerizing said halogenated hydrocarbon compound in the presence of said catalyst composition.

8. The process of Claim 4 wherein the fluorine distribution in a halogenated hydrocarbon compound is changed by disproportionating said halogenated hydrocarbon compound in the vapor phase in the presence of said catalyst composition.

9. The process of Claim 4 wherein the fluorine content of a halogenated hydrocarbon compound is decreased by dehydrofluorinating said halogenated hydrocarbon compound in the presence of said catalyst composition.

10. The process of Claim 4 wherein the fluorine content of a halogenated hydrocarbon compound is decreased by reacting said halogenated hydrocarbon compound with hydrogen chloride in the vapor phase in the presence of said catalyst composition.

11. A method for preparing a composition comprising the crystalline cobalt-substituted alpha-chromium oxide of Claim 1, comprising:

(a) co-precipitating a solid by adding ammonium hydroxide to an aqueous solution of a soluble cobalt salt and a soluble trivalent chromium salt that contains at least three moles of nitrate per mole of chromium in the solution and has a cobalt concentration of from about 0.05 mole % to about 6 mole % of the total concentration of cobalt and chromium in the solution; and after at least three moles of ammonium per mole of chromium in the solution has been added to the solution;

(b) collecting co-precipitated solid formed in (a);

(c) drying the collected solid; and

(d) calcining the dried solid.

12. The method of Claim 11 wherein the soluble cobalt salt is a divalent cobalt salt.

13. The method of Claim 12 wherein the soluble cobalt and chromium salts are nitrates or hydrated nitrates

14. The method of Claim 12 wherein more than three moles of ammonium nitrate per mole of chromium is present in the aqueous solution.

TITLE

COBALT-SUBSTITUTED CHROMIUM OXIDE COMPOSITIONS, THEIR PREPARATION, AND THEIR USE AS CATALYSTS AND CATALYST PRECURSORS

ABSTRACT

A crystalline alpha-chromium oxide where from about 0.05 atom % to about 6 atom % of the chromium atoms in the alpha-chromium oxide lattice are replaced by trivalent cobalt (Co^{+3}) atoms is disclosed. Also disclosed is a chromium-containing catalyst composition comprising as a chromium-containing component the crystalline cobalt-substituted alpha-chromium oxide; and a method for preparing a composition comprising the crystalline cobalt-substituted alpha-chromium oxide. The method involves (a) co-precipitating a solid by adding ammonium hydroxide to an aqueous solution of a soluble cobalt salt and a soluble trivalent chromium salt that contains at least three moles of nitrate per mole of chromium in the solution and has a cobalt concentration of from about 0.05 mole % to about 6 mole % of the total concentration of cobalt and chromium in the solution; and after at least three moles of ammonium per mole of chromium in the solution has been added to the solution, (b) collecting the co-precipitated solid formed in (a); (c) drying the collected solid; and (d) calcining the dried solid.

Also disclosed is a chromium-containing catalyst composition comprising a chromium-containing component prepared by treating the crystalline cobalt-substituted alpha-chromium oxide with a fluorinating agent; and a process for changing the fluorine distribution (i.e., content and/or arrangement) in a hydrocarbon or halogenated hydrocarbon in the presence of a catalyst. The process involves using as the catalyst a composition comprising the crystalline cobalt-substituted alpha-chromium oxide and/or the treated cobalt-substituted alpha-chromium oxide.

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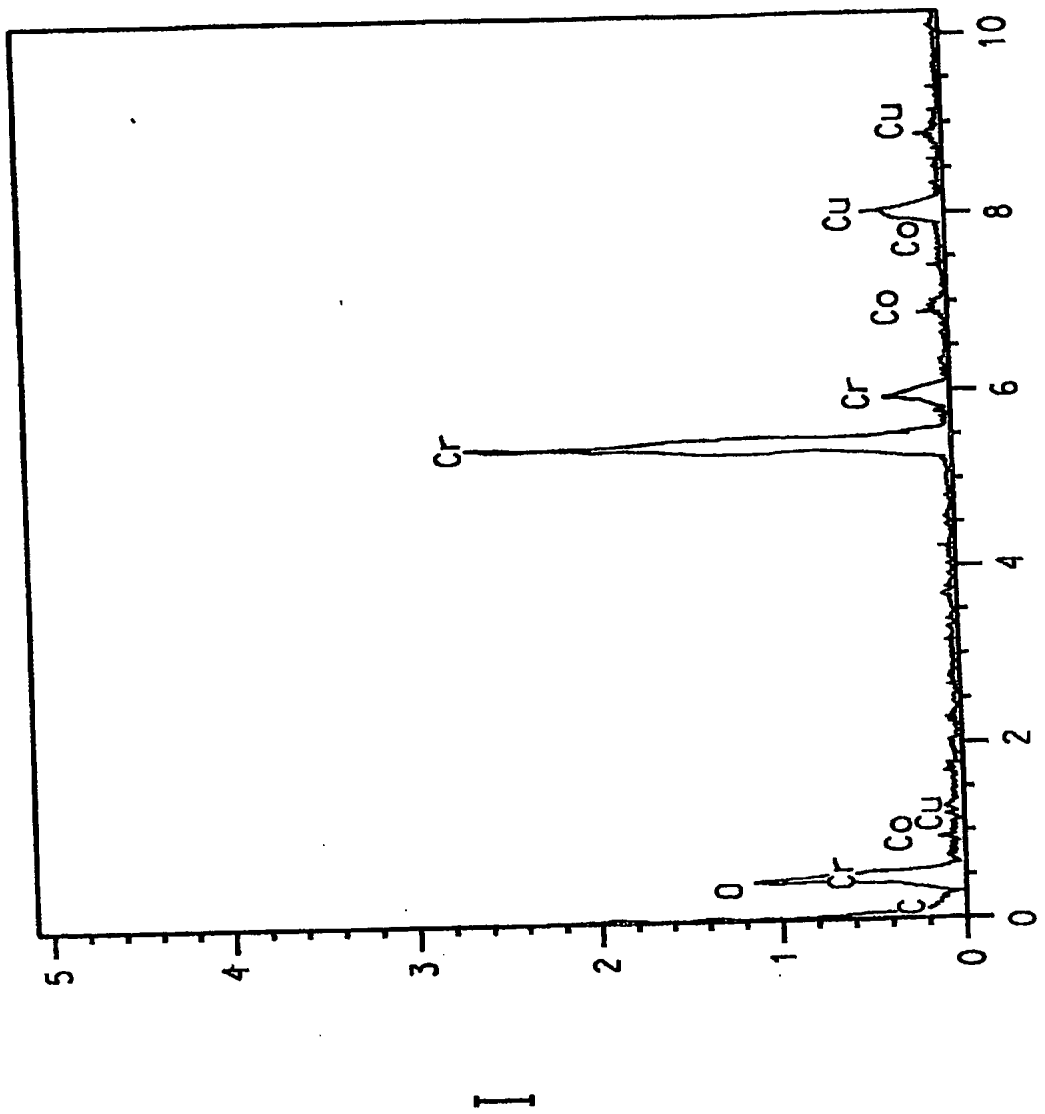


FIG. 1

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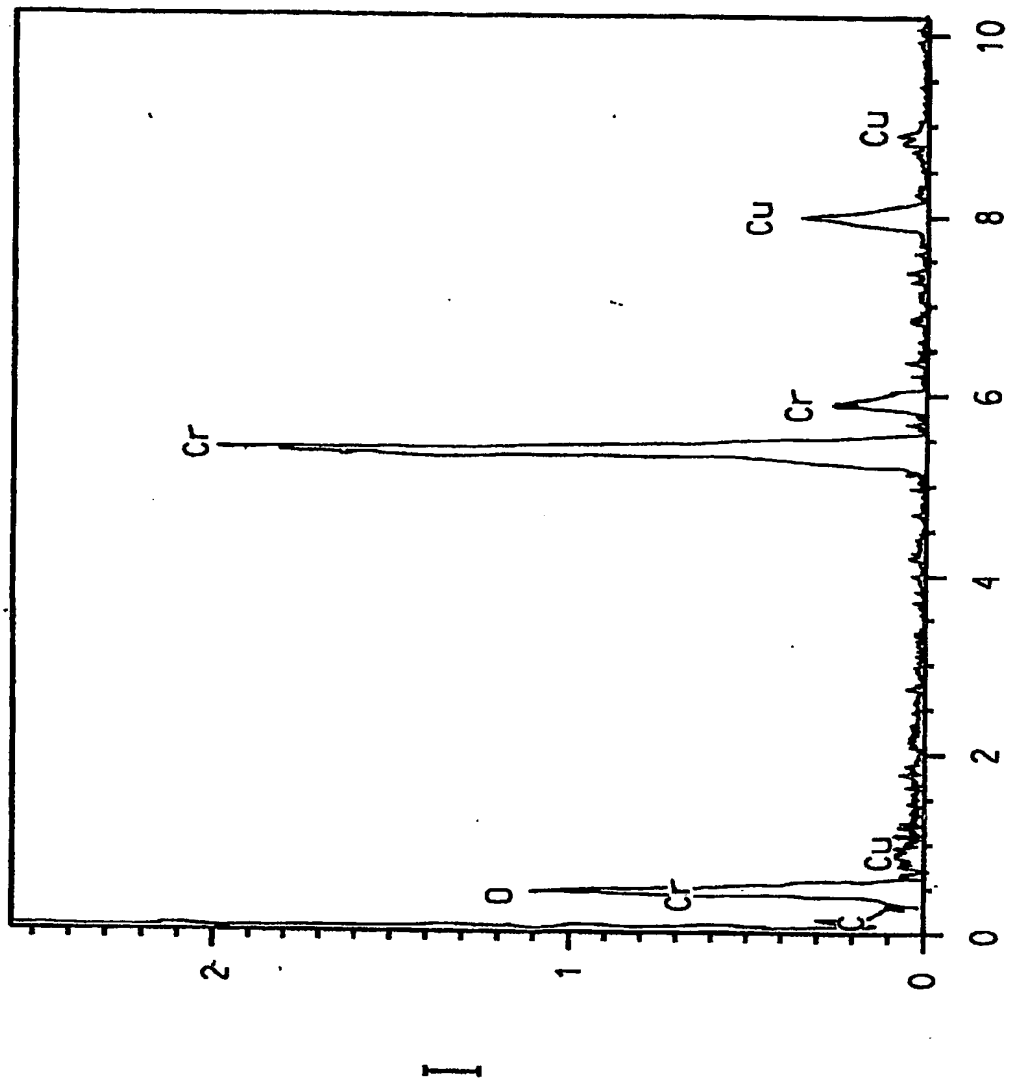


FIG. 2

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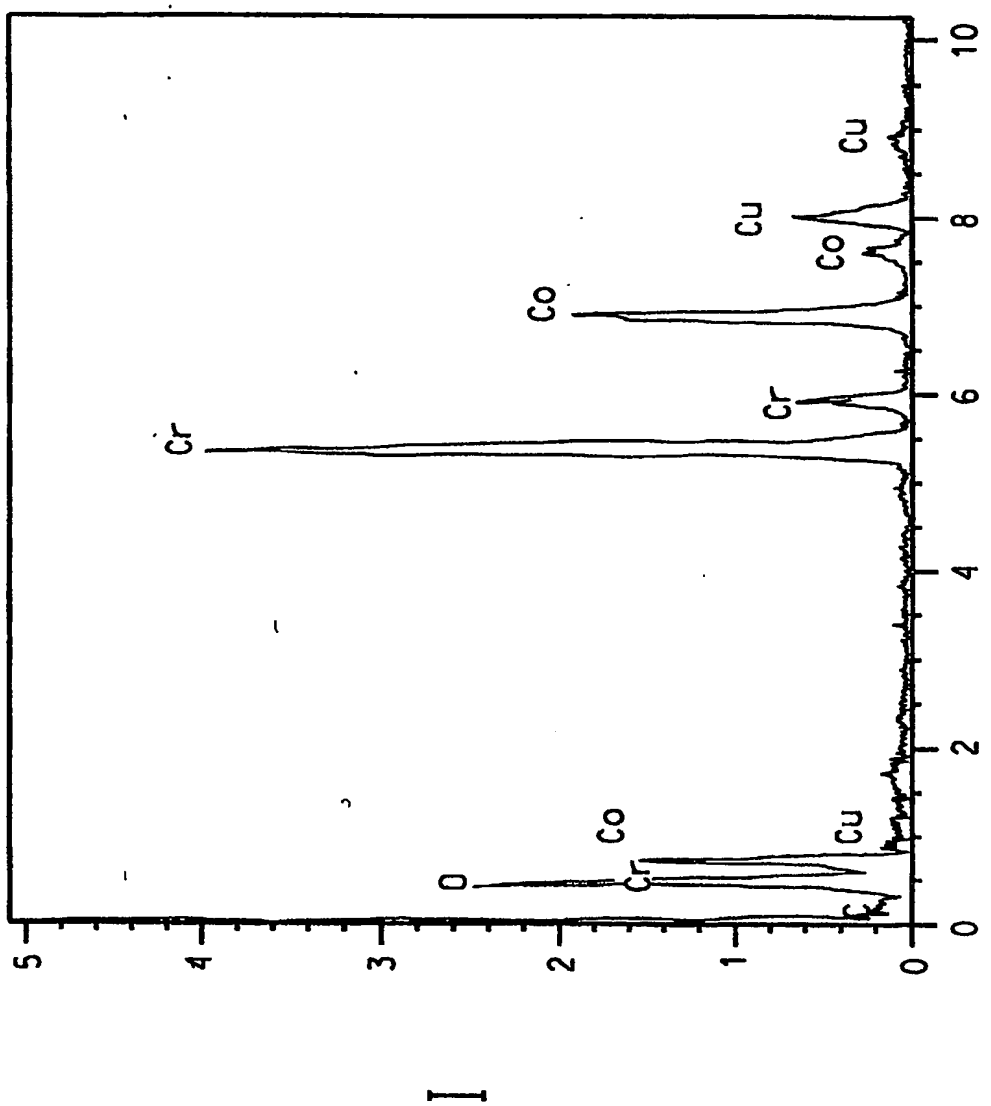


FIG. 3

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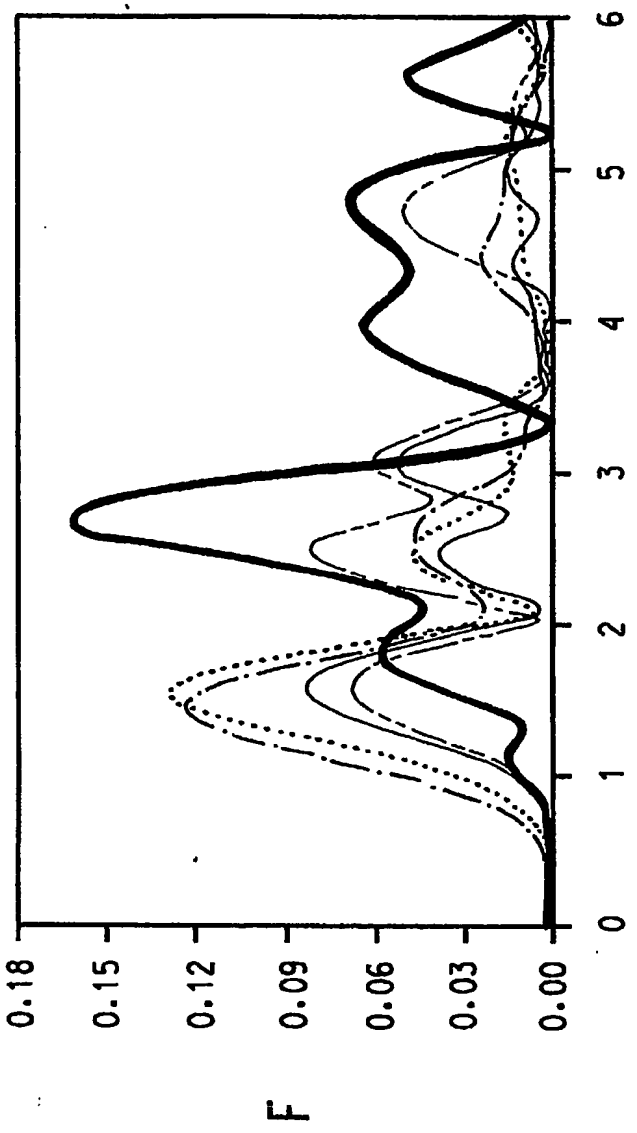


FIG. 4